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Ionic Pairs in PPA-Modified Bitumen: Insights from Model Compounds

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Abstract

The reaction between polyphosphoric acid (PPA) and bitumen is ill understood. To help define possible reactions, model compounds, isoquinoline and 1-methyl-2-quinolinone, were reacted with PPA. Both compounds formed salts with PPA. An infrared study of the salts revealed that PPA releases a terminal proton, as opposed to an internal one, and that with isoquinoline, the charges of the ionic pair are localized, but stabilized by bound water. With 1-methyl-2-quinolinone, the charges are delocalized and stabilized by resonance. This study demonstrates that ionic pairs need an environment of high dielectric constant to form in bitumen.

Introduction

Polyphosphoric acid (PPA) is a mixture of phosphoric acid (PA) oligomers, whereas bitumen, sometimes called asphalt cement, is a complex mixture of hydrocarbons with polar compounds that contain sulphur, nitrogen, or oxygen, if not all three heteroatoms.[1] Bitumen is used in civil engineering applications where it sometimes flows and deforms in service under the heat of summer. In an effort to raise viscosity and reduce this flow, it is sometimes modified with PPA,[2,3] typical PPA concentrations being 0.2% to 1.2% by weight of bitumen. PPA reduces or eliminates foaming problems encountered when concentrated phosphoric acid (PA), which contains 15% water, is used to modify bitumen.[4]

Several reactions have been proposed to explain the stiffening effect of PPA on bitumen,[2-5] but given the various bitumen sources and heteroatom compositions,[6,7] much uncertainty remains as to the type and the extent of the reactions. These reactions might be with aromatic nuclei, nitrogen, oxygen, or sulphur functional groups, or all of them together.

A greater understanding of the reaction between PPA and bitumen may be obtained by working with model compounds that carry organic functional groups identified in bitumen and petroleum fractions[8- 11]. Here, we report on the reaction between PPA and two functional groups, namely, pyridine and pyridinone. For this purpose, isoquinoline and 1-methyl-2-quinolinone were used as model compounds (Figure 1). The reaction between PPA and the model compounds was monitored by infrared spectroscopy. The findings indicated that both organic functional groups form ion pairs with PPA, but not through the same pathway.

Experimental Section

The reactants were used as received (Table 1). PPA, or PA, and the model compounds were mixed in conditions as close as possible to those used to mix PPA and bitumen. The model compounds were thus selected for their high boiling temperatures. For the reaction, the acid was stirred with an excess of isoquinoline, or 1-methyl-2-quinolinone, and heated at 150ºC. A weight ratio of 1:5 (acid:model) provided enough potential new product for their separation and analysis. In a typical experiment, 0.2 g of liquid PPA was weighed in a 4 mL vial and 1 g of model compound was added. After closing the vial with a septum cap, argon was blown over the mixture through a needle. A venting time of 5 min at a flow rate of 2 mL/min allowed for flushing out moisture and oxygen. This flushing was meant to prevent any undue oxidation of the model compound during heating. After venting, the mixture was heated for 1h and then allowed to cool to room temperature.

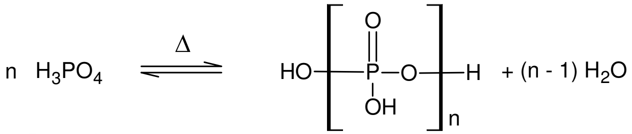
Crystalline products were isolated by filtration. Acetone was used to remove unreacted isoquinoline and chloroform was used to remove 1-methyl-2-quinolinone. The solid products were dried and ground with KBr before they were pressed into a disk for FTIR analysis. Fifty infrared scans at a resolution of 4 cm^{-1} were obtained on a Bomem MB100 spectrophotometer between 4000 cm^{-1} and 400 cm^{-1}. The transmission spectra were normalized to the most intense aromatic C–H absorbance near 3055 cm^{-1}.

Results and discussion

Reaction of isoquinoline. Isoquinoline and PPA were immiscible liquids at room temperature. Upon heating, they remained immiscible and no colour change was observed. No reaction was apparent and an infrared spectrum of the isoquinoline upper layer taken immediately after its cooling showed that it had remained immiscible and unaffected by PPA during heating. After standing for about 2h at room temperature, however, visual observation revealed that white crystals had developed, the volume of which increased over about one day. Interestingly, upon mixing isoquinoline and phosphoric acid, crystals formed immediately and no heating was required. Phosphoric acid is less viscous than PPA and viscosity may play a role in the rate of crystal formation, but other factors must be at play because without the initial heating to 150ºC the crystallization of an isoquinoline-PPA salt was much slower. It started after about 48 h and crystallization continued for about a week.

The infrared spectrum of the crystalline product revealed that the slow reaction of PPA and isoquinoline (IQ) was not simply a protonation of the type IQ + PPA-OH → $IQH^{+}PPAO^{-}$ (Figure 2). The salt showed a broad absorbance at 3429 cm^{-1}, at the left of the aromatic C–H stretches between 3000 cm^{-1} and 3200 cm^{-1}. The 3429 cm^{-1} absorbance was unexpected. It is often assigned to phenols,[12] which would have indicated that the isoquinoline ring was substituted by an OH group of PPA. This was consistent with absorbances at 2300-2800 cm^{-1}, 1700-1800 cm^{-1} and 850-900 cm^{-1} that could be assigned to an OH substituted pyridine rings,[13] but the absence of C–O absorbances in the mid and far IR denied the possibility of a phenolic structure.

From a comparison of the spectrum of the isoquinoline salt with spectra of hydrated and unhydrated pyridine salts,[14] the 3429 cm^{-1} absorbance was assigned to bound water, along with a broad band centered near 1730 cm^{-1}. The origin of this water was perplexing given its absence in isoquinoline and the initial flushing of moisture and oxygen from the reaction vessel. The 3429 cm^{-1} absorbance indicated that water was produced during the reaction between isoquinoline and PPA, which is consistent with the dehydration of phosphoric acid or the lengthening of the PPA chain during heating[1] as shown in Reaction 1. The production of water and its complexation with the isoquinoline-PPA salt was also consistent with the kinetics of salt formation. As indicated earlier, a salt with PPA only formed slowly without heating to 150ºC, and it formed quickly with concentrated phosphoric acid, which contains 15% of free water by weight.[15]



Reaction 1

The IR region between 1800 $cm^{-1}$and 3000 cm^{-1} relate to PO–H and N^+–H stretching.[12-14] The frequency of the N^+–H stretching in protonated pyridine is 1800-2200 cm^{-1}, where a broad doublet of weak to medium intensity is found.[14] In the PPA-isoquinoline salt, the N^+–H stretch partially overlaps with that for PO–H stretch normally at 2100 cm^{-1} to 2700 cm^{-1}. To distinguish the two stretches, the salt with PPA was compared to a salt with PA (Figure 3). The salt with the smaller anion, PA, showed a doublet of peaks at 1931 cm^{-1} and 2035 cm^{-1}, some 100 cm^{-1} lower than the salt with PPA, with absorbances at 2003 cm^{-1} and 2132 cm^{-1}. In pyridine salts produced with anions of decreasing sizes, the N^+–H absorbance shifts to lower frequencies.[13] Consequently, the doublet at 1931 cm^{-1} and 2035 cm^{-1} in the isoquinoline-PPA salt was attributed to the N^+–H stretching of the isoquinoline ring.

As expected, the protonation of the isoquinoline nitrogen led to some shifts in IR frequencies related to ring motions (Table 2). Of greatest interest, however, were the absorbances shown by the salt, but absent from the spectrum of isoquinoline. In this respect, new absorbances at 1654 cm^{-1} and 1394 cm^{-1} were noted (top of Figure 4). Based on the C=C stretching of substituted quinolines[16] between 1652 cm^{-1} and 1658 cm^{-1}, the 1654 cm^{-1} band was assigned to C=C stretching. Similarly, based on ring stretching at 1390-1370 cm^{-1} in naphthalenes,[12] the 1394 cm^{-1} absorbance was attributed to the stretching of the protonated isoquinoline double ring system. Both new infrared absorbances indicated that in terms of ring motions, the pairing of isoquinoline with PPA was similar to ring substitution through a covalent bond.

PPA is a mixture of oligomers with 2 to 14 repeat units,[1] indicated by *n* in Reaction 1. The several PO–H stretches between 2200 cm^{-1} and 3000 cm^{-1} in Figure 3 suggest that several OH groups, or environments, exist in the PPA salt. This is consistent with the existence of non-equivalent OH groups in PPA oligomers as illustrated in Figure 5. This is also the case with concentrated PA, which contains monomeric, dimeric and trimeric PA in an approximate ratio of 85:14:1.[17] To avoid confusion, these *n*-mers are called ortho-, pyro- and tri-phosphoric acids. Hence, the PO–H absorbance peaks at 2642 cm^{-1} and 2678 cm^{-1} in Figure 3 were attributed to equivalent PO–H groups in the isoquinoline-orthophosphoric acid salts. The much weaker absorbance of the isoquinoline-PPA salt was consistent with the relative concentrations of orthophosphoric acid in PPA and PA[1,17]. The absorbance at 2430 cm^{-1} was attributed to the internal OH of the dimeric pyrophosphoric acid, whereas the shoulder at 2363 cm^{-1} was attributed to hydroxyls at least three phosphorus atoms away from the pyridine ring (Figure 5). These assignments are also consistent with distinct O–P=O groups.

The mixture of oligomers in PPA also leads to various O–P=O environments in salts with isoquinoline as shown by the multiplicity of P=O and P–O stretching absorbances between 850 cm^{-1} and 1350 cm^{-1} (bottom of Figure 4). In this region, the strong PPA bands completely occluded weak isoquinoline bands. The P=O stretching absorbance of neat PPA is very broad and strong, with a maximum near 1210 cm^{-1}. In the salt with isoquinoline, the P=O stretch is split into several bands that all occur at higher frequencies. An increase in frequency is attributed to a neighbouring electronegative group that inductively withdraws electrons,[12] which is consistent with the pull of a positively charged nitrogen in proximity to the P=O group. In the PPA salt, the broad P=O band with three maxima between 1250 cm^{-1} and 1325 cm^{-1} indicates that at least three different P=O groups along the PPA chain experience various degrees of inductive pull from a single positive charge. The farthest the cation from the double bond, the lesser is its inductive effect and the smaller is the P=O frequency shift away from its initial position of 1210 cm^{-1} (Figure 6). If there were several charges, say one per PA repeat unit, the P=O groups of the various oligomers would likely be closer together, not dispersed over more than 100 cm^{-1}. It was therefore concluded that in the salt with isoquinoline, each PPA oligomeric chain binds with only one isoquinoline molecule.

The effect of the cation on the P–O stretch is consistent with the shift in the P=O frequency. Terminal and internal P–O frequencies respectively show at 939 cm^{-1} and 1031 cm^{-1} in PPA (bottom of Figure 4). With the pyridinic cation in proximity, the internal P–O frequency of PPA is raised by 12 cm^{-1} to a single peak at 951 cm^{-1}, whereas the terminal P–O frequency at 1031 cm^{-1} in PPA is raised by 37 cm^{-1} to 141 cm^{-1} in several peaks between 1070 cm^{-1} and 1200 cm^{-1}. The larger frequency shift of the terminal P–O over that of the internal P–O indicates a greater electron pull of the N$^+$–H cation on the terminal P–O (Figure 6). This demonstrates that isoquinoline salts form at the end of the PPA chains, not in the middle, most likely because of steric constraints. As with the P=O frequencies, the multiplicity of peaks reveals that PPA oligomers of different lengths form a salt with isoquinoline.

Reaction of 1-methyl-2-quinolinone (M2Q). M2Q is a solid that did not dissolve in PPA at room temperature. Upon heating, M2Q melted, but two immiscible layers were observed, with PPA at the bottom. After an hour of heating, the hot upper M2Q layer was drawn out of the reaction vessel, and an FTIR spectrum was acquired. The spectrum was a simple overlap of 1-methyl-2-quinolinone with some PPA, which revealed that PPA had dissolved into the melted M2Q without causing a reaction. Upon cooling the mixture to room temperature, however, a white gel-like material gradually formed, and after 24h a white solid was obtained. Obviously this solid may have been crystallized

M2Q, but it was insoluble in ethyl ether or chloroform, in contrast to M2Q. FTIR of the solid revealed that it was a salt of PPA, with typical PPA bands as in the spectra of Figures 3 and 4. No water was visible, contrary to isoquinoline.

In contrast to the salt with isoquinoline, the M2Q-PPA salt was not obtained by protonation of the ring nitrogen, but through the ketone. This is clearly demonstrated by the loss of the ketone absorbance in the infrared spectrum of Figure 7. Neat M2Q showed a strong and asymmetrical absorbance with a maximum at 1650 cm^{-1}. The asymmetry arose from the overlap of three absorbances, namely those of an α,β-unsaturated ketone, a lactam ketone and an alkene. These groups absorb at 1685±20 cm^{-1}, 1670±10 cm^{-1} and 1615±35 cm^{-1}, respectively, with the alkene absorbance being much weaker that the other two.[12] Upon the protonation of M2Q by PPA, the ketone absorbances disappeared completely to unveil the absorbance of the unsaturation at 1627 cm^{-1}.

Amides have a resonance structure due to the delocalization of the lone nitrogen pair of electrons on the nitrogen.[12] The distinct protonation behaviour of M2Q with respect to isoquinoline resides in the resonance structure from both the amide and the unsaturated ketone (Figure 8, top line). The amide resonance leads to an aromatic ten pi-electron naphthalenic structure (A) and an increased electron density at the lactam oxygen. The resonance of the unsaturation also increases the electron density at the oxygen (structure B). The combined absence of a free electron pair on the nitrogen (A) and the high electron density around the oxygen (A, B) favoured the protonation of the oxygen, not the nitrogen, as shown in Figure 8 by structures C-E. All three protonated structures are in resonance, but structure E is likely favoured by the additional hydrogen-bonding of the enol hydroxyl hydrogen with nitrogen, and it explains the loss of C=O absorbance upon protonation. Moreover, the positive charge in structure E can be further delocalized through the aromatic ring (structure F). This ring delocalization is consistent with the disruption of phenyl absorbances in going from M2Q to the salt. The ortho-substituted ring absorbance,[12] at 754 cm^{-1} in M2Q, is shifted up to 765 cm^{-1} (not shown), and the phenyl band at 1500 cm^{-1} is shifted up to 1523 cm^{-1} (Figure 7). The most noteworthy change however, resides in the loss of the phenyl doublet[12,13] at 1584 cm^{-1} and 1594 cm^{-1} upon the protonation of M2Q. This loss of absorbance possibly arises from a symmetrical distribution of the positive charge around the ring, with the symmetry rendering the absorbance IR inactive.

Ionic pairs in PPA-modified bitumen. In media with dielectric constants below 15, PPA must be a very weak acid because the charges that result from dissociation cannot readily be stabilized.[1] The dielectric constant (ε) of bitumen is about 3,[18] consequently, it was hypothesized that PPA could only dissociate and react with bitumen in enclaves of high dielectric constants.[1] The results obtained here support this view.

Isoquinoline is a fairly strong base as far as petroleum bases are concerned. It is therefore not surprising that it would form a salt with PPA. With a low ε = 11 for isoquinoline, however, the salt did not form readily. It is only through a complex with water (ε = 79), obtained by heating PPA, that the NH^+PPA^- ionic pair was stabilized and that a salt slowly formed. With consideration for lower concentrations, as will be discussed later, a similar scenario can be envisaged for the reaction of PPA with other bitumen bases.

In contrast to isoquinoline, the formation of a salt of 1-methyl-2-quinolinone and PPA could hardly have been predicted. Amides do not normally act as bases because of the resonance of the lone electron pair on nitrogen,[12] and α,β-unsaturated ketones are weak acids.[19] Notwithstanding, the formation of a salt with PPA is evidence that the combination of the two organic functions lead to an enolate type of structure, as shown in the upper line of Figure 8. The enolate readily coupled with PPA, most likely because the dielectric constant of 1-methyl-2-quinolinone is greater than 15 and because PPA could more readily dissociate to release a proton. The exact dielectric constant of 1-methyl-2-quinolinone is unknown, but based on values for N-naphthenylenylacetamide (ε= 24) and pyridine-oxide (ε=36), which has charges not dissimilar to that of structure A in Figure 8, the dielectric constant of M2Q may be near 30. It may further be postulated that the formation of a 1-methyl-2-quinolinone-PPA salt was facilitated by the stabilization of the charges around the aromatic ring (Figure 8). As a result, there was no need for a hydration sphere, and indeed no water was visible in the infrared spectrum.

The concentration of heteroatomic compounds in bitumen is low. The weight content of nitrogen is usually less than 1 percent, as it is with oxygen.[6] Consequently, the reaction of PPA with bitumen cannot produce solid salts. We have postulated before that PPA would react with bitumen in enclaves relatively high in heteroatomic content.[1] Based on the work here, it can be further postulated that ionic pairs are produced, and that these pairs are stabilized in a nano environment relatively rich in heteroatomic content.

Conclusion

Polyphosphoric acid is often reacted with bitumen to raise its viscosity and reduce its flow. Due to the complexity in the composition of bitumen, it is difficult to determine the nature of the reaction between them. To help define possible reactions, two bitumen model compounds were reacted with PPA in conditions close to those used with bitumen. The first compound, isoquinoline, had a pyridine functional group, whereas the other coupound, 1-methyl-2-quinolinone, had a pyridinone functional group. Both model compounds formed solid salts with PPA.

The FTIR study of the salts revealed that PPA oligomers acted as monoprotic acids that released a proton from a terminal hydroxyl group, as opposed to an internal one. The study also revealed the different nature of the salts. In a medium of low dielectric constant, i.e., isoquinoline, the charges of the ionic pair were localized, but stabilized by bound water that arose from the dehydration of PPA during heating. In the medium of higher dielectric constant, i.e., 1-methyl-2-quinolinone, the charges were delocalized and stabilized by resonance so that no hydration was necessary.

Given a low concentration of functional groups in bitumen, a solid salt phase would likely be replaced by dispersed ionic pairs upon reaction with PPA. As this study indicates, these ionic pairs would need an environment of high dielectric constant. Other bitumen functional groups may be present in this environment. Consequently, we will report later on the reaction of PPA with other functional groups.

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Captions

Table 1. Characteristics of the Reactants

Table 2. Infrared Ring Absorbances in Isoquinoline (IQ) and its Salt*

Figure 1. Compounds used in this study.

Figure 2. Infrared spectra of PPA, isoquinoline (IQ), and their salt between 4000 cm^{-1} and 1800 cm^{-1}.

Figure 3. PO–H and N^+–H region of the IR spectrum for isoquinoline (IQ) salts with PPA and with PA.

Figure 4. Fingerprint region of interest in the infrared spectra of PPA, isoquinoline, and its salts with PPA and PA. For clarity, the upper portion does not show the IQ-PA salt.

Figure 5. Salts of phosphoric acids with different PPA chain lengths.

Figure 6. Illustration of the inductive pull of the positive charge on the P=O and P–O groups along a PPA chain and trends in frequency shifts. The size of the arrows illustrate the relative strength of the pull.

Figure 7. Carbonyl and aromatic region of M2Q and its salt. The spectra were normalized to the ortho-aromatic absorbance near 760 cm^{-1}.

Figure 8. Resonance structures in protonated and unprotonated M2Q.

Table 1. Characteristics of the Reactants[a]

	PA	PPA	IQ	M2Q
source[b]	Anachemia	ICL	SA	ABCR
purity/grade	85% PA	115% PA	97 wt %	99 wt %
b.p. (ºC)	158	> 158	242	325
CAS[c]	7664-38-2	8017-16-1	119-65-3	606-43-9

[a] PA, phosphoric acid; PPA, polyphosphoric acid; IQ, isoquinoline; M2Q, 1-methyl-2-quinolinone. [b]ICL, ICL Performance Products LP; SA, Sigma-Aldrich; ABCR, ABCR GmbH & Co KG. [c] CAS: chemical abstract service number

Table 2. Infrared Ring Absorbances in Isoquinoline (IQ) and its Salt [a]

	IQ	IQ-PPA[b]
aromatic ring	1627, 1498	**1654**, 1625, 1498
pyridine ring	1589, 1576, 1558	1599, 1566, 1552
naphthalenic ring	1382,638, 482	**1394**, 1382, 638,478
ortho substituted ring	1141, 1029, 821	hidden, 1029, 827
ring breathing	945	hidden
ortho substituted pyridine	827, 742	821, 752

[a] Assignments based on compilations (12, 13)

[b] Bold markings indicate new bands.

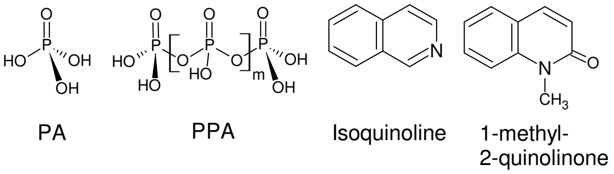

Figure 1. Compounds used in this study.

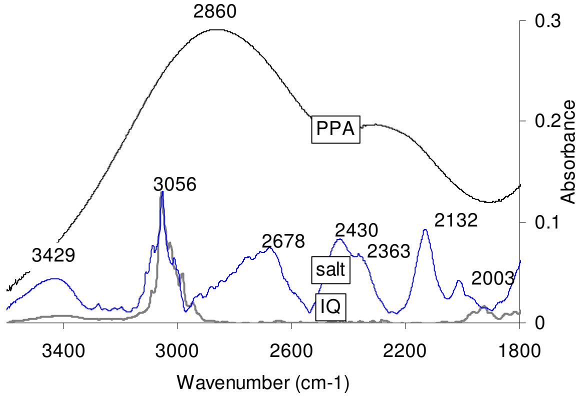

Figure 2. Infrared spectra of PPA, isoquinoline (IQ), and their salt between 4000 cm^{-1} and 1800 cm^{-1}.

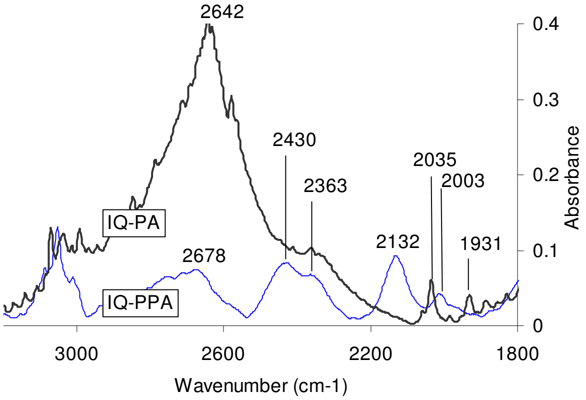

Figure 3. PO–H and N^{+}–H region of the IR spectrum for isoquinoline (IQ) salts with PPA and with PA.

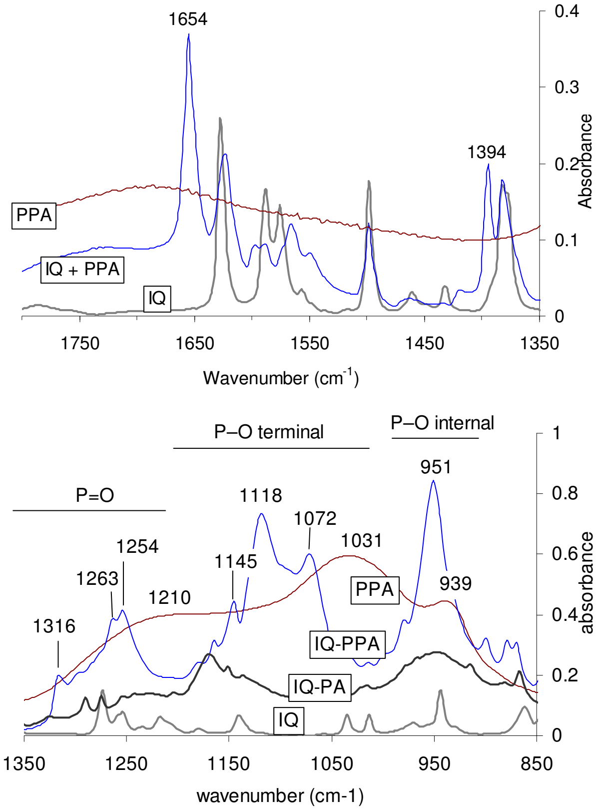

Figure 4. Fingerprint region of interest in the infrared spectra of PPA, isoquinoline, and its salts with PPA and PA. For clarity, the upper portion does not show the IQ-PA salt.

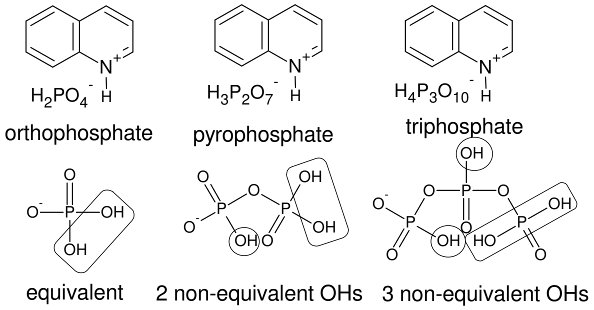

Figure 5. Salts of phosphoric acids with different PPA chain lengths.

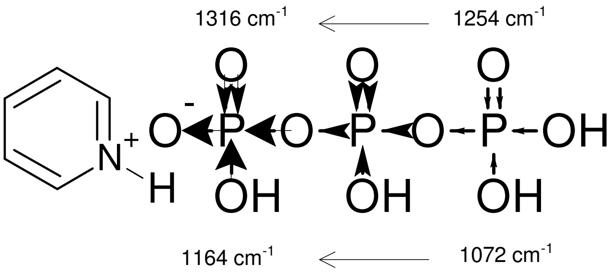

Figure 6. Illustration of the inductive pull of the positive charge on the P=O and P–O groups along a PPA chain and trends in frequency shifts. The size of the arrows illustrate the relative strength of the pull.

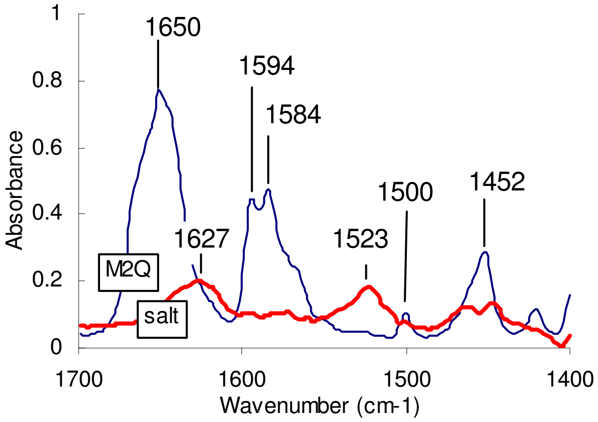

Figure 7. Carbonyl and aromatic region of M2Q and its salt. The spectra were normalized to the ortho-aromatic absorbance near 760 cm^{-1}.

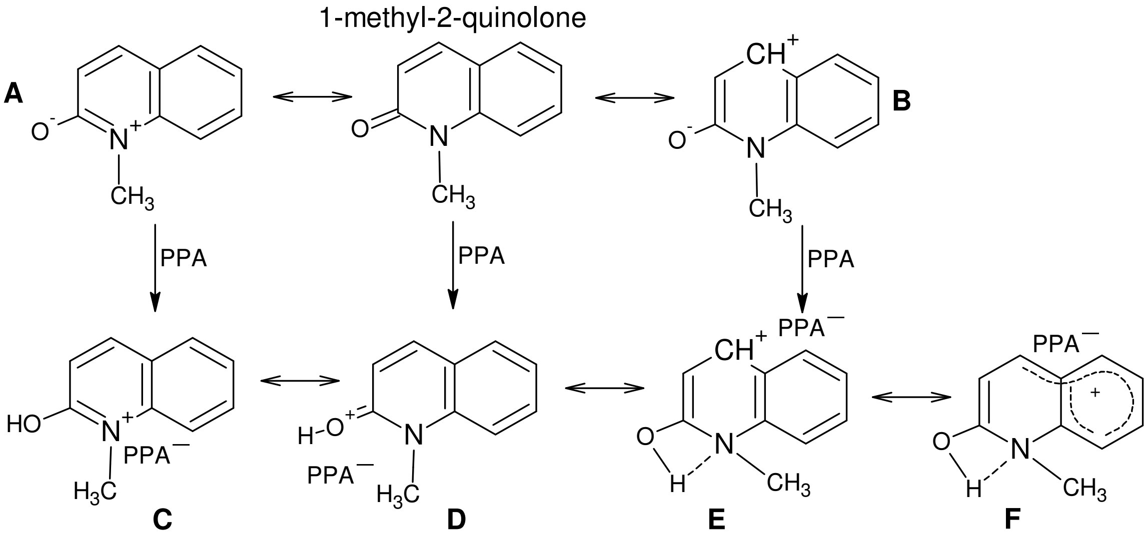

Figure 8. Resonance structures in protonated and unprotonated M2Q.