

Spectroscopic and theoretical investigation of capillary-induced keto–enol tautomerism of phenacyl benzoylpyridinium-type photoinitiators

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Abstract: Phenacyl benzoylpyridinium (PBP) salts are effective photoinitiators for cationic polymerization. In this study, it is shown that PBP salts are stable in their keto forms, and undergo a reversible keto–enol tautomerization reaction when a capillary action is applied. Spectroscopic and theoretical methods are used to explain the existence of the enol forms in the capillary tube.

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Keywords: phenacylium salts; keto–enol tautomerization; capillary effect; TDDFT

INTRODUCTION

Light-induced polymerization has attracted increasing interest in the last few decades because industrial applications concern several different areas such as surface coatings, microelectronics, adhesives and printing inks.^{1–6} Although the majority of the growing interest deals with free radical polymerization,^{2,5} much effort has been devoted to cationic polymerization.^{1,7–9} Various families of initiators used in the photoinitiation of cationic polymerizations are based on the use of certain onium salts^{1,9} such as diphenyliodonium,^{10,11} alkoxy pyridinium¹² and triphenylsulfonium¹³ salts.

Rapid advances in cationic polymerization have been made possible by the development of initiators, or initiator and co-initiator combinations, having enough wavelength flexibility for various formulations. Such flexibility for photoinitiated cationic polymerization using onium salts has been achieved by photosensitizers,^{9,14,15} charge transfer complexes¹⁶ and free radicals.^{17–19} However, the use of systems of more than one component for photoinitiation may not be so successful due to some unresolved problems such as solubility and compatibility of the components and high costs. Among one-component initiators, dialkylphenacyl sulfonium salts hold considerable promise for the future as a means of photolysis at high wavelengths and strong protonic acid generation.²⁰

We recently reported that phenacyl anilinium (PA)^{21–23} and phenacyl benzoylpyridinium (PBP)²⁴ salts are effective photoinitiators for cationic polymerization of cyclohexene oxide. We proposed that the initiation mechanism is quite different from that of dialkylphenacyl sulfonium salts. In contrast to the corresponding sulfonium salts, they undergo irreversible photolysis upon irradiation according to Scheme 1.

Both homolytic and heterolytic cleavages eventually yield the same initiating species.

It was also observed that PBP salts showed different absorption characteristics, i.e. absorption within the visible range. Spectroscopic investigations revealed that this difference stems from the structural characteristics of PBP salts and their reversible keto–enol tautomerization.

Recently, it was demonstrated that *N*-phenacyl pyridinium salts can be easily converted into ylides.²⁵ The methylene protons in *N*-alkyl pyridinium salts of the type $\geq N^+ - CH_2 - Y$ are acidic, where *Y* is a strong electron-withdrawing substituent, and their reactivity becomes comparable with that of the methylene group of 1,3-dicarbonyl compounds. The pK_a values of a number of *N*-phenacyl pyridinium salts are in the range 7–10.9.^{26,27} Strong bases can abstract one of such protons, which may lead to the formation of ylides.^{28–33} On the other hand, in pyridinium-type ylides, the stability of such compounds is enhanced by delocalization of the charge into the heterocyclic ring. Deprotonation of *N*-phenacyl pyridinium halides with strong bases such as DABCO,³⁴ 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 7-methyl-1.5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD)³⁵ proved the participation of pyridinium ylides.

Here we report further experimental observations and theoretical calculations for the tautomerization reaction of PBP salts.

EXPERIMENTAL

The PBP salts were synthesized according to the method reported previously.²⁴

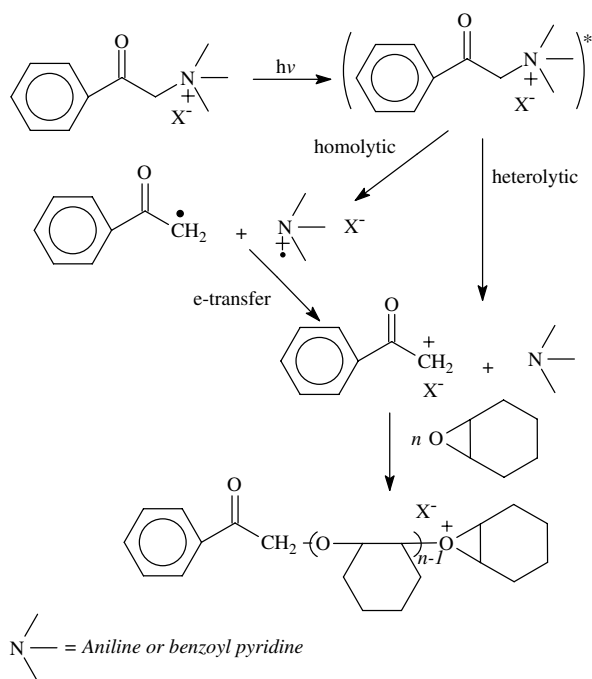
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Scheme 1. Photoinitiated cationic polymerization of cyclohexene oxide by phenacyl anilinium (PA) salts.

UV-visible spectra were recorded using a UV-1601 Shimadzu spectrophotometer. ^1H NMR spectra were recorded using a Bruker 250 MHz spectrometer with *d*-acetonitrile as the solvent and tetramethylsilane as the internal standard. Fourier transform infrared (FTIR) spectra were recorded using a Perkin-Elmer FTIR Spectrum One spectrometer.

THEORETICAL CALCULATIONS

The geometries of keto and enol forms were optimized using the density functional theory (DFT) method with B3LYP hybrid functional³⁶ at the 6-31g(d) level. The Gaussian 2003 software package³⁷ was used for the theoretical calculations. The molecules optimized had (+1) charge because of the counterion in the solution. IR vibrational frequencies for the closed-shell systems in their ground states were calculated. The first 20 lowest-lying excited states were optimized using the time-dependent DFT (TDDFT) method, and UV absorption frequencies and the oscillator strengths of the corresponding transitions were calculated. The intensities were calculated from the oscillator strengths and normalized to 1. For the solvent calculations, each molecule was re-optimized in the presence of the polar solvent acetonitrile ($\epsilon = 36.64$) and nonpolar solvent tetrahydrofuran (THF) ($\epsilon = 7.58$) using the polarizable continuum model (PCM)^{38,39} implemented in Gaussian 2003 at the B3LYP/6-311++g** level. All energies given in the tables are zero-point-corrected energies at 298 K.

RESULTS AND DISCUSSION

All the PBP salts listed in Table 1 have a similar structure to that of *N*-phenacyl pyridinium halides.

However, their keto–enol tautomerization reaction in organic phase has quite different characteristics. PBP salts are in two forms. In their solid state, PBP salts prefer the keto form. However, a mixture of most likely keto form and a small amount of enol form may be present in organic solvents such as acetonitrile, acetone and dimethylsulfoxide (DMSO), but the enol form could not be identified by spectroscopic techniques like UV, IR and NMR due to its very low concentration. After capillary action was applied, the concentration of the enol tautomers formed within the capillary were high enough for detection by UV spectrophotometry.

The structural characterization of the keto form of PBP salts was carried out using ^1H NMR. The spectrum of molecule **1a** exhibited one singlet at 6.39 ppm due to the methylene group (Fig. 1). For the other geometrical isomers, **1b**, **1c** and **1d**, the same peak was shifted to lower field and observed at 6.26, 6.28 and 6.18 ppm, respectively (Table 2).

The UV wavelengths corresponding to maximum absorbance of the keto and enol forms of PBP salts are given in Table 2. It can be seen that the enol form absorbs in the visible region whereas the keto form absorbs in the UV region. UV spectra (Fig. 2) indicate that the position of the precursor benzoyl group in the pyridine ring affects the absorption characteristics of the enol form. A higher absorption maximum at 507 nm is observed for the enol tautomers (**2a** and **2c**) in which the benzoyl group is at the 4-position. This behavior is attributed to the better electron

Table 1. Structure of PBP salts

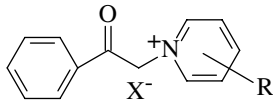
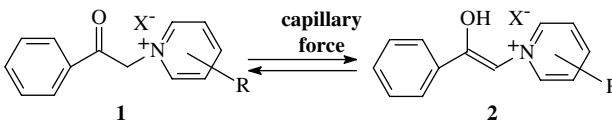
		
Compound	R	X [−]
1a	4-COC ₆ H ₅	PF ₆ [−]
1b	3-COC ₆ H ₅	PF ₆ [−]
1c	4-COC ₆ H ₅	SbF ₆ [−]
1d	H	SbF ₆ [−]

Table 2. ^1H NMR chemical shifts (ppm) of PBP salts in *d*-acetonitrile and UV absorption maxima of keto forms in the solid state and enol forms in acetonitrile

					
R: COC ₆ H ₅ , H X [−] : PF ₆ [−] , SbF ₆ [−]					
Entry	Compound (keto form)	Chemical shift (ppm)	λ_{max} (nm)	Compound (enol form)	λ_{max} (nm)
1	1a	6.39	252	2a	507
2	1b	6.26	252	2b	442
3	1c	6.28	253	2c	507
4	1d	6.18	248	2d	438

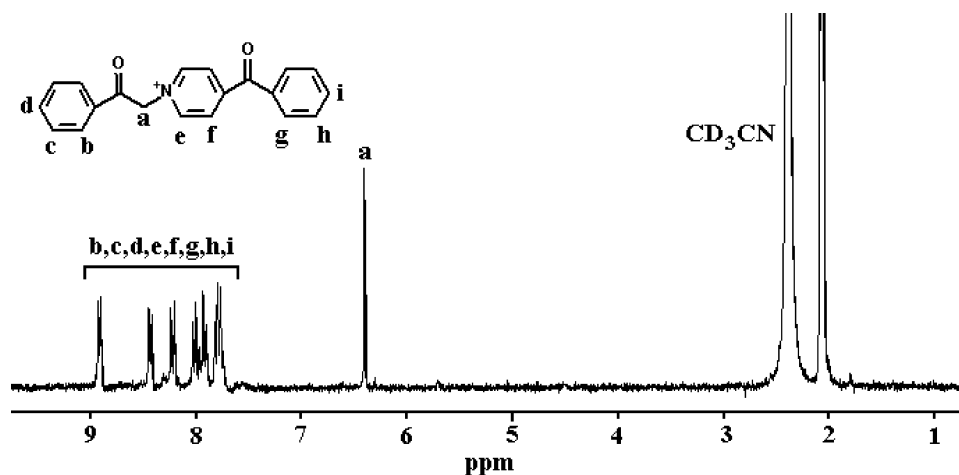


Figure 1. ^1H NMR spectrum of *N*-phenacyl-4-benzoylpyridinium hexafluorophosphate in *d*-acetonitrile.

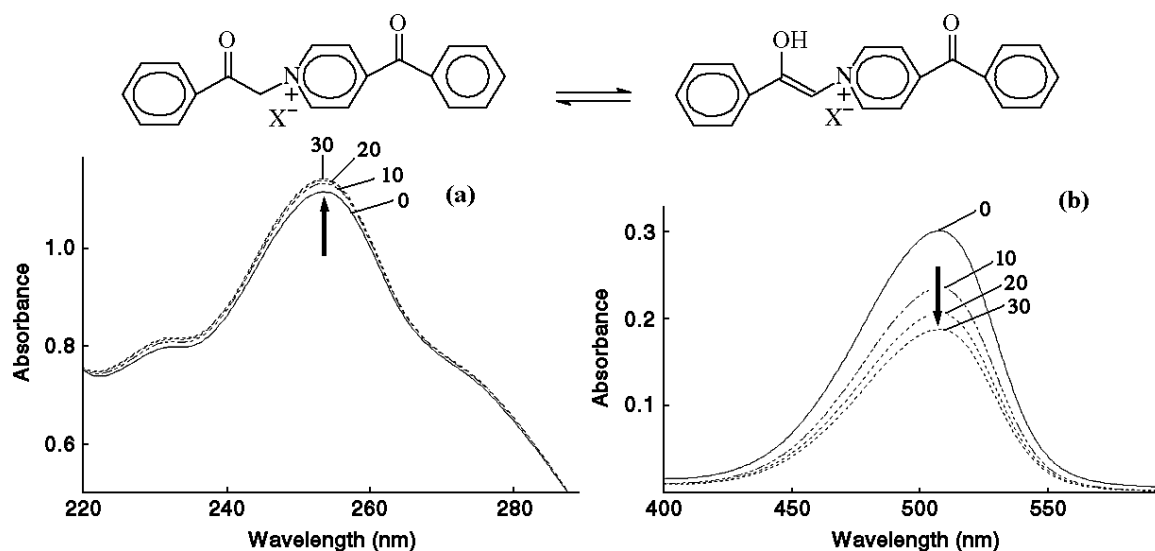


Figure 2. UV spectral changes of salts **1a** and **2a** upon irradiation at $\lambda > 507$ nm under nitrogen in acetonitrile. Salt concentration is $2.4 \times 10^{-5} \text{ mol L}^{-1}$. The spectra were obtained at 10 min intervals.

delocalization on the aromatic ring and lower steric hindrance. Considering the 3-positions of the benzoyl group in the pyridine ring, the absorption maximum of the enol form (**2b**) is rather low (442 nm) compared to **2a** and **2c**. In the case of no substitution in the pyridine ring (**1d**), the enol form (**2d**) has the lowest absorption peak at 438 nm among the synthesized PBP salts.

The theoretical calculations were done only for **a**- and **b**-type salts in both tautomeric forms. The effect of the position of the benzoyl group attached to the pyridine ring on the structure and in the IR and UV spectra was discussed. The B3LYP/6–31g** optimized geometries are given in Table 3. It can be seen that, depending on the position of the benzoyl group, the molecule is either almost linear or bent. In **b**-type salts, connection of the benzoyl group to the pyridine ring through the 3-position deviates the geometry from linearity, and the geometry plays a very important role in their photoinitiating capacities. It has been reported that this capacity is larger for linear molecules since their interaction with monomeric units

to be polymerized becomes easier because of the lower steric hindrance.²⁴

Theoretically calculated UV spectra (Fig. 3) reveal that the transition in the keto forms takes place mainly between $\pi \rightarrow \pi^*$ molecular orbitals localized on the backbone atoms of the unsymmetric acetophenone groups observed at 254 nm (**1a**) and 266 nm (**1b**), whereas the main transition in the enol forms is due to transitions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) observed at 393 nm (**2a**) and 383 nm (**2b**). The peaks due to $\pi \rightarrow \pi^*$ transitions observed in the keto forms are observed in the same region at wavelengths of 246 nm (**2a**) and 237 nm (**2b**) but with smaller intensities in the enol tautomers (Table 4).

Absorption spectra of the keto and enol forms of **a** and **b** look similar if no solvent effect is considered. The keto forms have only one maximum in the UV region but the enol forms have two maxima and the latter has a higher intensity and absorbs in the visible region (Fig. 3(a) and (e)). The first maximum

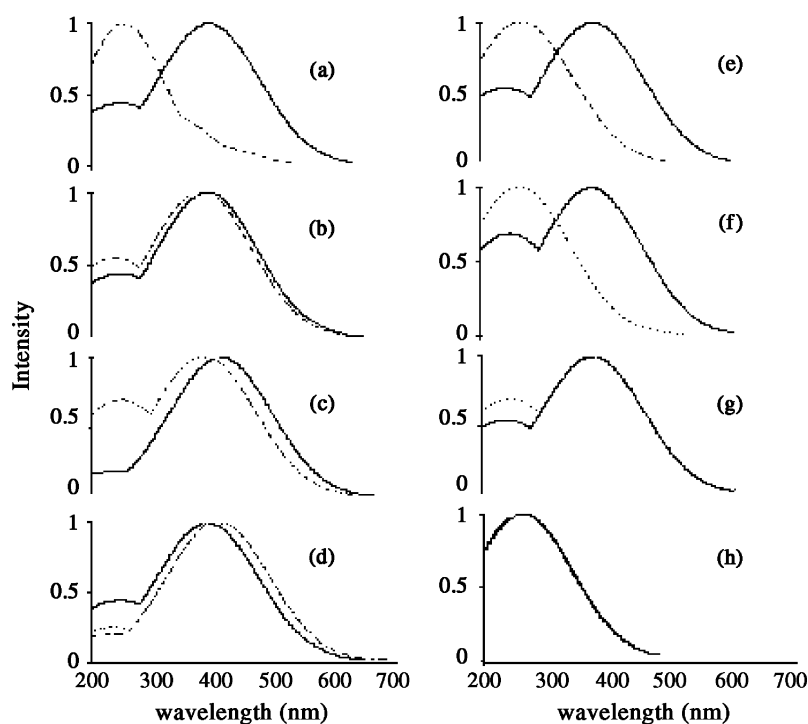


Figure 3. Theoretical UV spectra: (a) dashed line (**1a**), solid line (**2a**), no solvent; (b) dashed line (**2b**) no solvent, solid line (**2a**) no solvent; (c) dashed line (**2b**), solid line (**2a**), in acetonitrile; (d) dashed lines (**2a**), in acetonitrile and in THF, solid line (**2a**) no solvent; (e) dashed line (**1b**) no solvent, solid line (**2b**) no solvent; (f) dashed line (**1b**), solid line (**2b**), in acetonitrile; (g) dashed line (**2b**) in acetonitrile, solid line (**2b**) no solvent; (h) dashed line (**1b**) no solvent, solid line (**1b**) in acetonitrile.

Table 3. Optimized geometries of the studied salts

Compound	Optimized geometries: B3LYP/6-31G(d)
1a	
2a	
1b	
2b	

peaks of the enol forms are affected by the position of the benzoyl and they are more intense for **2b**

Table 4. Wavelengths of UV absorption maxima of the salts in the gas phase and in solvent

Compound	No solvent		Solvent acetonitrile		Solvent THF	
	λ^1_{\max} (nm)	λ^2_{\max} (nm)	λ^1_{\max} (nm)	λ^2_{\max} (nm)	λ^1_{\max} (nm)	λ^2_{\max} (nm)
1a (keto)	–	254	–	–	–	–
2a (enol)	246	393	238	413	244	412
1b (keto)	–	266	–	264	–	–
2b (enol)	237	383	248	385	–	–

(Fig. 3(b)). This intensity difference is even greater in acetonitrile. It becomes less intense for **2a** and more intense for **2b** (Fig. 3(c) and (g)). The second maximum peak in the visible region is mainly due to the HOMO–LUMO transition and shifts slightly to higher wavelengths for both molecules in the enol form (Fig. 3(d)). HOMO localizes on the hydroxyl group and naturally one can expect that the acidic proton of the –OH group is affected by the polarity of the medium whose $\varepsilon > 0$, and exhibits a red shift. It is clear that the UV absorption behavior of PBP salts changes depending on the solvent. The polarity of the solvent does affect the frequency of the peak observed in the visible region. The discrepancy between the experimental and theoretical absorption wavelengths is attributed to the solvent effect and possibly they are underestimated by the method used. The solvent calculations were repeated with larger basis up to the 6-311++g(d,p) basis set, but no further improvement was achieved in the maximum absorption wavelengths.

Because of the solvent-dependent red shifts in the visible region, it is rational to assume that the amount of red shift could be increased up to the experimental values if the solvent were explicitly included in the modeling or solvent effects were calculated in a better way. The important result for us is that the enol forms of the PBP salts absorb at higher wavelengths than the keto forms in the experimental spectra as well as in the theoretical spectra. The observed shifts in the wavelength maxima are more than 100 nm in both cases. The peak corresponding to the $\pi \rightarrow \pi^*$ transition is observed at larger wavelengths in the keto forms than the enol forms of the molecules. This result is also consistent with the fact that the thermodynamic stability of the keto forms is higher or their total electronic energy is smaller than that of the enol forms given in Table 4. The response of the PBP salts in solvents arises from the hydroxyl group present, so the UV absorption spectra of the keto forms do not show any changes because of the solvent (Fig. 3(f) and (h)).

The theoretical IR spectra of the salts (Figs 4 and 5) show that the peaks observed at 3705 and 1712 cm^{-1} for **2a** and peaks observed at 3714 and 1754 cm^{-1} for **2b** are the O–H and C=C stretching frequencies which are characteristic vibrational responses only for the enol forms. In the IR spectra of keto forms, these peaks are absent.

All experimental and theoretical results showed that PBP salts undergo a reversible keto–enol tautomerization reaction when the capillary action is applied. Due to the strong adhesive forces between the solution and the glass and also due to the strong pressure difference inside the capillary tube and atmospheric pressure, the chemical equilibrium shifts towards the right, thus favoring the enol formation

within the capillary tube. Instant coloration of the solution indicates that the solution absorbs in the visible region and proves the formation of the enol form. The gas-phase Gibbs free energies calculated theoretically at room temperature showed that ΔG_r of the keto–enol tautomerization reaction is $10.4\text{ kcal mol}^{-1}$ for molecule **a** and $11.4\text{ kcal mol}^{-1}$ for molecule **b** (Tables 5 and 6). The equilibrium constants were calculated from the Gibbs free energies and found to be 2.4×10^{-8} and 4.4×10^{-9} , respectively. When the solution is allowed to rise in the capillary tube, the colorless solution becomes colored. Upon releasing the colored solution back into the beaker, the color disappears slowly. Whenever the capillary force is applied, the transparent solution becomes colored again. The time for color disappearance depends on the concentration of the original salt solution and the concentration of the molecules passing into the enol form. The same behavior was observed in different solvents and no noticeable differences were seen in the color and in the time of color disappearance. It can be said that the driving force for tautomerization of these salts is not the solvent effect or the polarity of the solvent but the force created within the capillary tube.

Table 5. Calculated zero-point energy corrected total electronic energies and Gibbs free energies of the compounds at 298 K

Compound	Electronic energy (a.u.)	Gibbs free energy (a.u.)
1a	−976.428889	−976.479082
2a	−976.412667	−976.462559
1b	−976.429446	−976.479197
2b	−976.411216	−976.461087

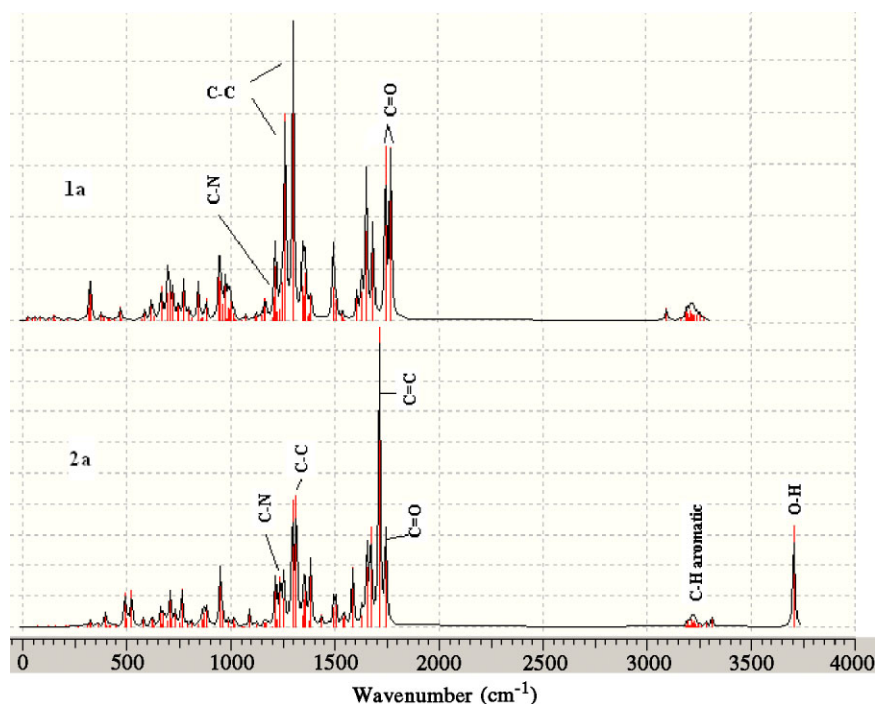


Figure 4. Theoretical IR spectra of **1a** and **2a**.

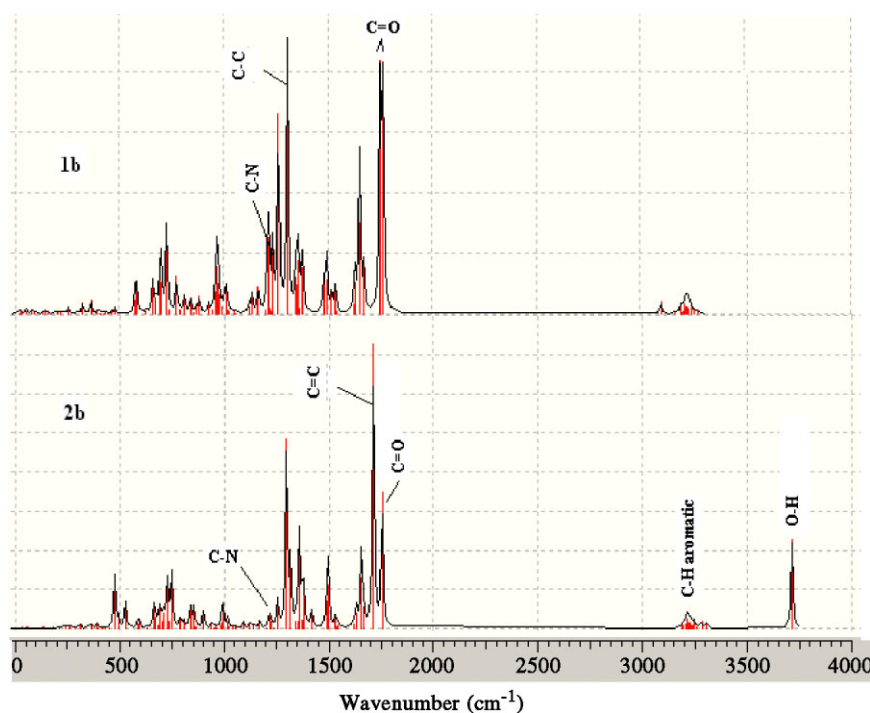


Figure 5. Theoretical IR spectra of **1b** and **2b**.

Table 6. ΔE and ΔG of keto \rightarrow enol tautomerization reaction at 298 K

Compound	ΔE_r (kcal mol ⁻¹)	ΔG_r (kcal mol ⁻¹)
a	10.2	10.4
b	11.4	11.4

CONCLUSIONS

PBP salts are a class of cationic photoinitiators with interesting absorption characteristics at $\lambda < 300$ nm and around 500 nm arising from their keto–enol tautomerization. Such characteristics make these salts potentially applicable to various curing formulations with a wide range of wavelength selectivity. In this work, the structural and spectroscopic behavior of keto and enol tautomers as well as the energetics of the tautomerization reaction were studied both experimentally and theoretically. We showed that PDB salts are stable photoinitiators in their keto forms, and that the chemical equilibrium (the equilibrium constants of which are very low) shifts to the right, thus favoring the keto–enol tautomerization reaction due to capillary action. The driving force for this reaction to occur is not the solvent effect but the force created within the capillary tube. Efforts were devoted to show that the color change is due to enol formation within the capillary tube. The experimental and spectroscopic observations are supported by high-level DFT calculations. Free energy calculations led to the conclusion that the barrier for the keto–enol tautomerization reaction is small and easily overcome by the capillary force. Solvent effects may change the UV absorption characteristics of the enol tautomers in the visible region but their absorption characteristics at $\lambda < 300$ nm remain the same.

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