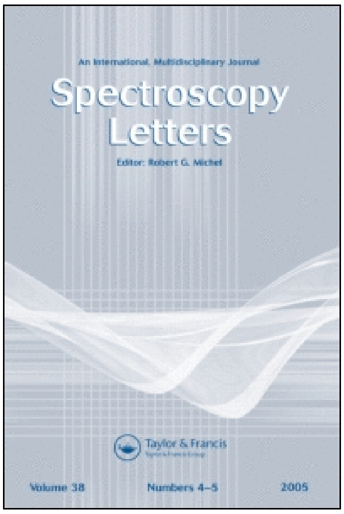

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Tautomerism in 1-Phenyl-3-Substituted Pyrazol-5-ones: FT-Infrared Spectral Analysis and *Ab Initio* Calculations

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To cite this Article Ivanova, B. B. , Chapkanov, A. G. , Arnaudov, M. G. and Petkov, I. K.(2006) 'Tautomerism in 1-Phenyl-3-Substituted Pyrazol-5-ones: FT-Infrared Spectral Analysis and *Ab Initio* Calculations', Spectroscopy Letters, 39: 1, 1 — 12

To link to this Article: DOI: 10.1080/00387010500437019
URL: http://dx.doi.org/10.1080/00387010500437019

Spectroscopy Letters, 39: 1–12, 2006
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ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010500437019

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Abstract: A comparative IR-spectral study of 3-phenyl-(DPhP) and 3-methyl-(MPhP) substituted 1-phenyl-pyrazol-5-ones both in solution and in the solid state was performed. It is shown that aprotic solvents stabilized the oxo (CH) tautomers, but the protic ones shifted the tautomeric equilibrium to the hydroxy (OH) forms. A zwitterion structure of MPhP in solid was determined to exist, rather than the CH-tautomer, DPhP. In addition, accompanying quantum chemical calculations (at the Hartree-Fock level of theory and with the 6-31G** basis set) suggest that the last phenomenon is a result of a steric hindrance caused by the bulky phenyl substituent at the 3-position of the pyrazolone ring.

Keywords: Ab initio calculations, IR-spectral study, 3-substituted 1-phenyl-pyrazol-5-ones, tautomerism

Received 22 January 2004, Accepted 2 December 2004

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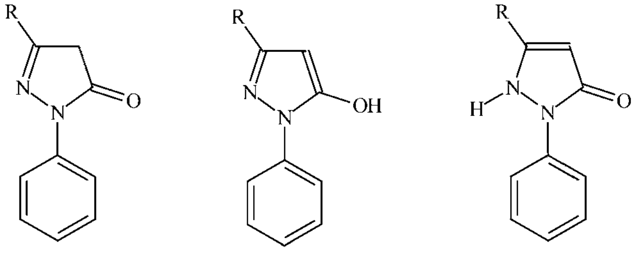
INTRODUCTION

Pyrazolone-5-one derivatives are an important class of heterocyclic compounds with wide scientific and technical application as materials,[1] in catalysis,[2,3] as precursors for CVD,[4] and potential antitumor medications.[5] Another range of uses is in the chemistry of dyes,[6,7] where stable color compounds are obtained by the insertion of specific conjugated substituents to the pyrazolone ring. On the other hand, the great ability for complexation with transition metals, because of the availability of electron-rich donor centers, brings its complexes to use in analytical chemistry,[1] pharmacology,[5] and in full-color organic EL displays.[8] The pyrazol-5-ones exhibit three basic tautomeric forms (Scheme 1) whose stabilization depends on the influence of the substituents and on the medium.[9−11] In the solid state, the discussed compounds subsist mainly in OH (Scheme 1, **2**) or NH form (Scheme 1, **3**),[12−17] with the priority of the last one.[10,12,15] As a rule, both OH and NH forms and more rarely CH-tautomers (Scheme 1, **1**) are stabilized through intramolecular hydrogen bond formation or complexation with the assistance of suitable substituents in the 3- and 4-position, respectively.[18−21]

A comparative infrared spectral study of the tautomerism of MPhP and DPhP pyrazol-5-one in solution and in the solid state is illustrated in the current study, while the results are completed with IR-spectral data of the protonated derivatives of the corresponding compounds. Additionally, a theoretical analysis including the heats of formations of the possible tautomers, their dipole moments and effective atom charges, all obtained by *ab initio* calculations on a large basis set (6-31G**) and Hartee-Fock level of theory, is performed. The results are an extension of our previous investigation, where both UV[22] and IR spectral studies[23] of the photoinduced tautomerization of these compounds were reported.



(1) (2) (3)

R = CH_3, C_6H_5

Scheme 1. Basic tautomeric forms of pyrazol-5-ones.

MATERIALS AND METHODS

The synthesis of the DPhP and MPhP as well as of the hydrochloric salt of DPhP was described in Refs.[22,23] and Ref.[24], respectively.

The 1-phenyl-3-methyl- pyrazol-5-one hydrochloric salt was obtained as follows: 0.1954 g 1-phenyl-3-methyl-pyrazol-5-one was dissolved in 20 mL methanol, and 10 mL diluted HCl (10^{-1} M) was added. The white crystals that were formed after the evaporation of the solvents at room temperature were filtered, washed with methanol, and dried in air. Yield: 85%.

A Bomem-Michelson 100 served as the FTIR instrument, and 150 scans were performed for each IR spectrum achieving a resolution of $\pm 2\,cm^{-1}$. The IR spectra of 0.01 M DPhP solutions in acetonitrile, chloroform, carbon tetrachloride, and ethanol (Merck, Uvasol) were recorded using 0.01 cm KBr and CaF_2 cells, respectively. The solid-state samples were investigated as KBr pellets and repeated as a Nujol suspension.

The *ab initio* calculations were carried out using the Dalton[25] program set. The heats of formation and electronic potential distribution for all the tautomers studied were calculated after a full geometry optimization using the 6-31G** basis set at the Hartee-Fock level of theory. The corresponding data are listed in Table 1.

RESULTS AND DISCUSSION

The 4000–400 cm^{-1} IR spectrum of DPhP in carbon tetrachloride is published in Ref.[23], the analogous one of MPhP is shown in Fig. 1, (1). The absence of the bands belonging to the NH and OH-stretching frequencies

Table 1. The calculated values of heats of formations (ΔH_f, kcal/mol), dipole moments (D), and carbonyl oxygen and imino-nitrogen single atomic charges of the tautomeric forms of MPhP and DPhP

	Tautomeric forms			
	MPhP		DPhP	
	CH	OH	CH	OH
ΔH_f (kcal/mol)	14.44	15.75	24.47	27.74
Dipole moment (D)	3.06	2.05	3.19	2.01
Single atomic charges				
O	−0.5331	−0.4468	−0.5317	−0.4466
N	−0.0525	−0.1693	−0.0614	−0.1685

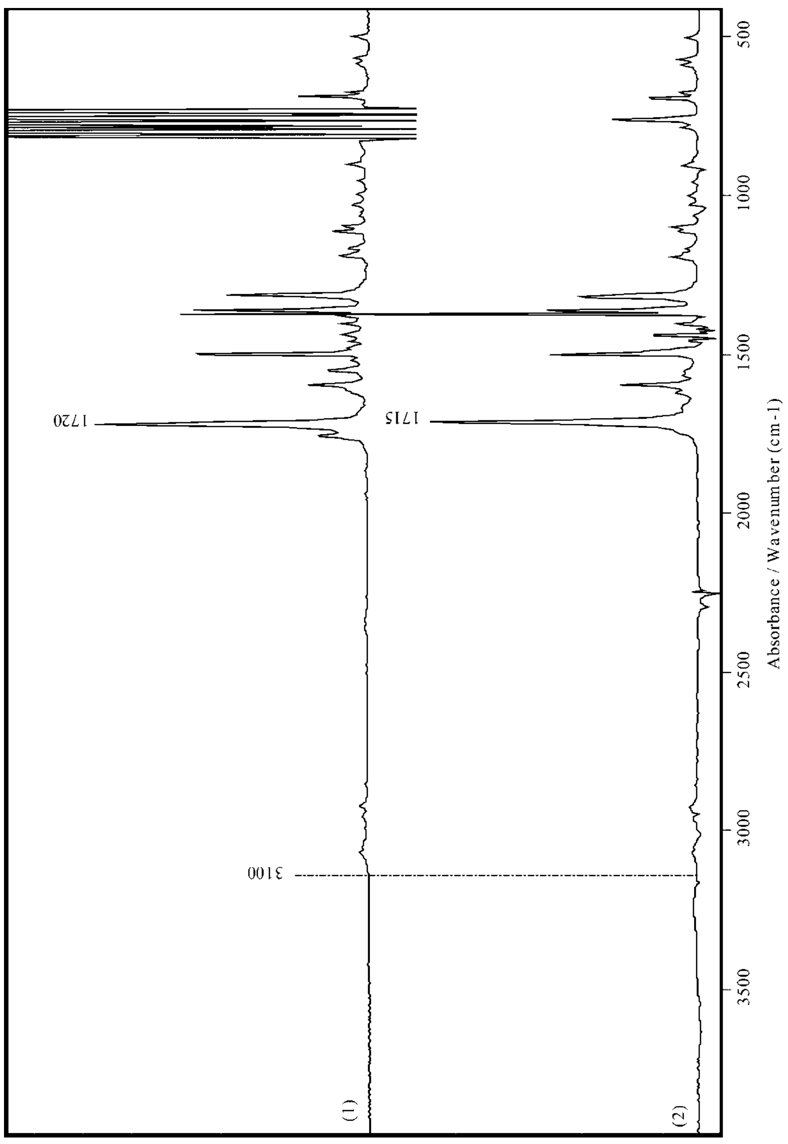


Figure 1. 4000–400 cm^{-1} IR spectra of MPhP in carbon tetrachloride (1) and acetonitrile (2).

over 3100 cm^{-1} indicates a stabilization of the CH-tautomer of both compounds (Scheme 1, **1**). The same data were obtained after dissolution in some other aprotic solvents; as an example, the IR-spectrum of MPhP in acetonitrile is given in Fig. 1, (2). These results illustrated the nonspecific solute-solvent interactions on the tautomeric equilibrium of the investigated 1-phenyl-pyrazol-5-ones. In terms of the polarity effect, the transition from carbon tetrachloride to acetonitrile as solvents was shown to be a difference between the dielectric constants $\Delta\varepsilon = 35.26$, which correspond to a variance at 41% regarding the normalized π^*-scale introduced by Kalmet and Taft.[26] All these data suggest a nonspecific solvent effect of acetonitrile provoking about a 10 cm^{-1} low-frequency shift of the stretching vibration of the polar C═O group (Figs. 2 and 3) and correlated well with the known data for some pyrazol-5-ones.[19]

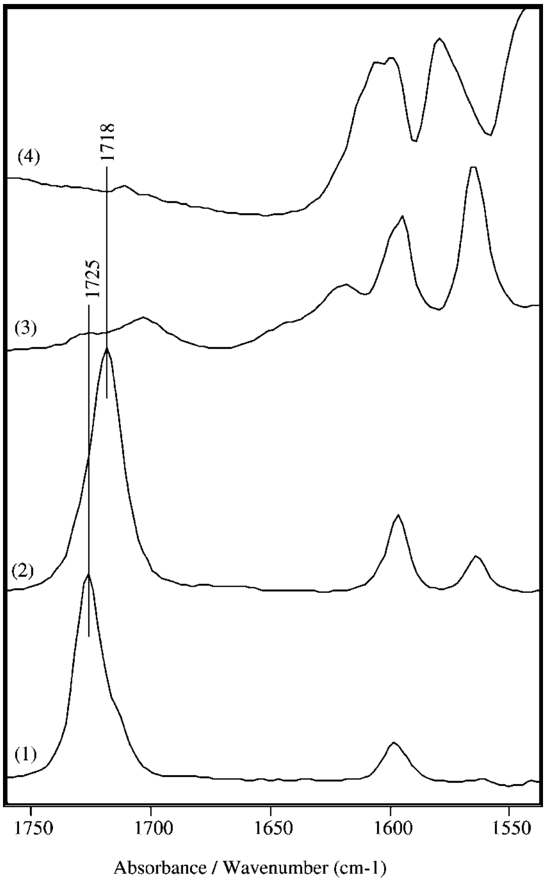


Figure 2. 1750–1530 cm^{-1} IR spectra of DPhP in carbon tetrachloride (1), acetonitrile (2), ethanol (3), and of its protonated form in solid state (4).

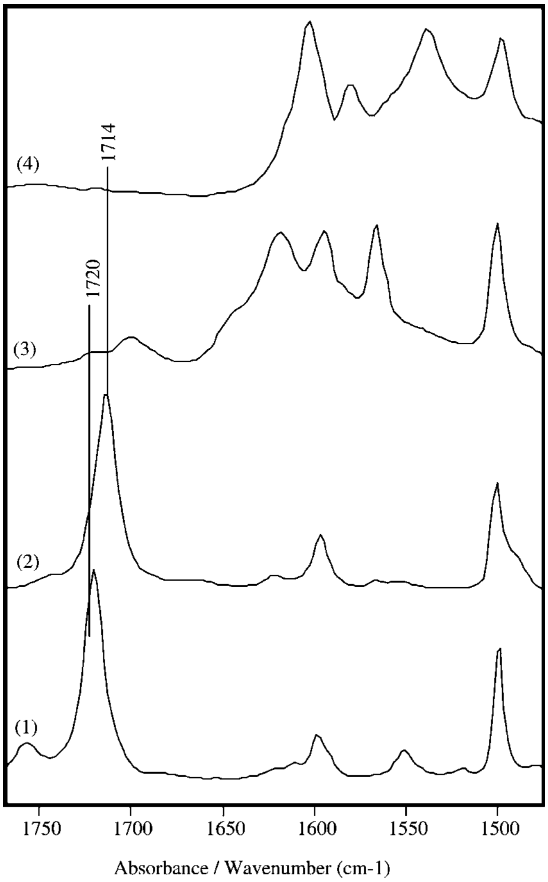


Figure 3. 1750–1530 cm^{-1} IR spectra of MPhP in carbon tetrachloride (1), acetonitrile (2), ethanol (3), and of its protonated form in solid state (4).

A different result is obtained after the dissolution of the studied compounds in methanol and ethanol. Figure 2, (3) and Fig. 3, (3) present the 1750–1550 cm^{-1} IR-spectra of an ethanol solution of DPhP and MPhP, respectively. In both cases, the intensive absorption maximum of the C=O stretching vibration over 1700 cm^{-1} is absent, thus indicating the establishment of one of the other tautomeric forms. Evidence about the priority of the NH- and OH-structure cannot be obtained by use of the corresponding stretching regions, because of the strong self-absorption of the alcohol solvents; nevertheless two results indicated the stabilization of the OH-tautomer.

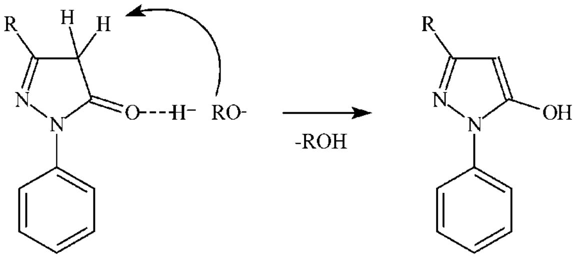
- The NH-structure consists of the conjugated C=O group (Scheme 1, **3**). This band should occur at about 1680 cm^{-1},[23] but it is absent from the spectra of Fig. 2, (3) and Fig. 3, (3).

- The protonated derivatives of DPhP and MPhP exist as OH forms (see below). In the 1750–1550 cm^{-1} range, the corresponding spectra are similar to those in ethanol solution (compare Figs. 2, (4) and 3, (4) with 2, (3) and 3, (3), respectively).

These results mean that the protic solvents methanol and ethanol appear to be weak acids (Scheme 2) and interact with the most negatively charged (see theoretical results stated below) oxygen atom of the carbonyl group, leading to tautomeric rearrangement and stabilization of the *enol*-form.

The last stated assumption correlated well with the known X-ray data about the structurally characterized OH-tautomer of 1-phenyl-3-methyl-pyrazol-5-one, obtained from the polar solvent mixture.[16] Moreover, an NH- and OH-forms equilibrium of DPhP in aqueous solution was determined in Ref.[27].

Surprising results in both DPhP and MPhP solid-state IR-spectra were observed (Fig. 4). The IR spectrum of DPhP [Fig. 4, (1)] is analogous to that of carbon tetrachloride,[23] indicating the presence of CH-tautomeric form. As was mentioned above, it is not typical of the 1-phenyl-pyrazol-5-ones in the solid state where the OH tautomers are preferred and additionally stabilized by intermolecular hydrogen bonding.[16] This phenomenon is realized by the building of the MPhP supramolecular structure. Its IR spectrum does not exhibit absorption maxima in the NH–, OH–, and C=O-stretching regions, but a wide intense band between 3200 and 2000 cm^{-1} is available [Fig. 4, (2)]. The last one is characteristic of the NH^{+}-stretching frequencies of the protonated amino group in amino acids where the C=O-stretching band also disappears because of the zwitterion nature in the solid state. Similar supposition was mentioned first in Ref.[28]. The last analogy suggests a similar dipolar disposition in the MPhP as a result of a strong OH...N (imino) intermolecular bond formation and next a proton transfer (Scheme 3). The IR spectrum of the MPhP-hydrochloride confirms the discussed structure. (Scheme 3, **3**). The restoration of the OH-group leads to the appearance of a new absorption maximum at about 3360 cm^{-1} assigned to the OH stretching frequency [Fig. 5, (2)]. The



Scheme 2.

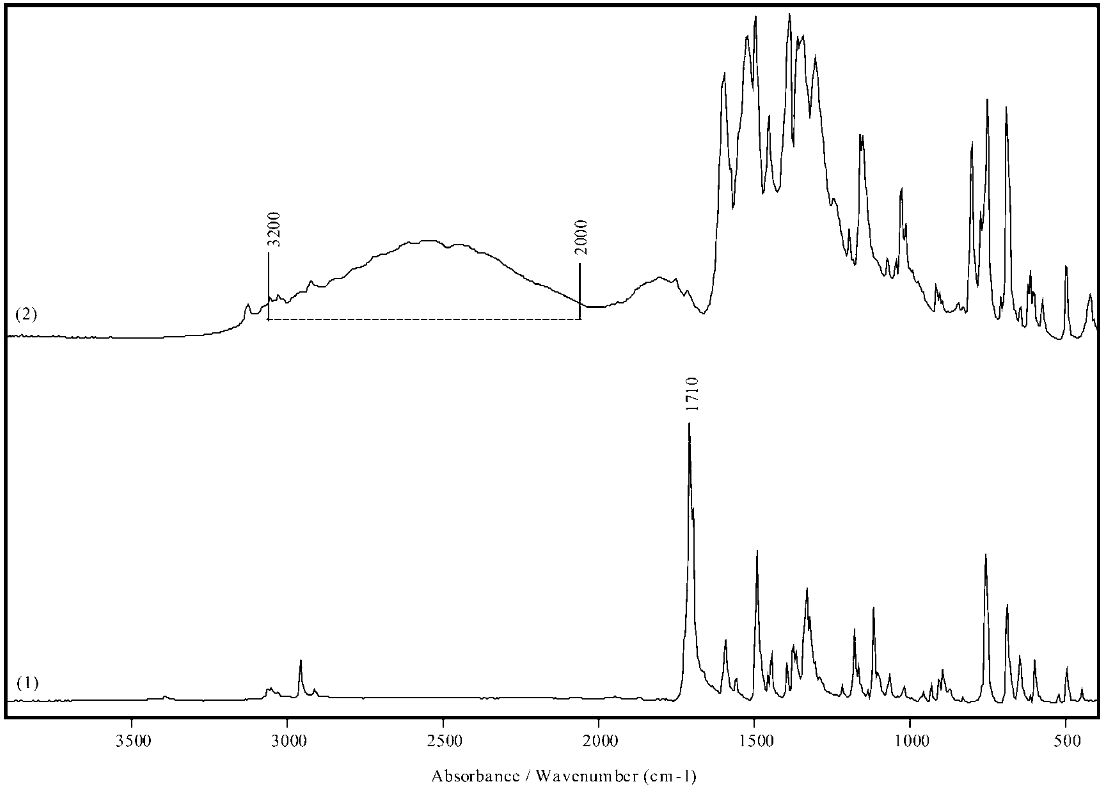
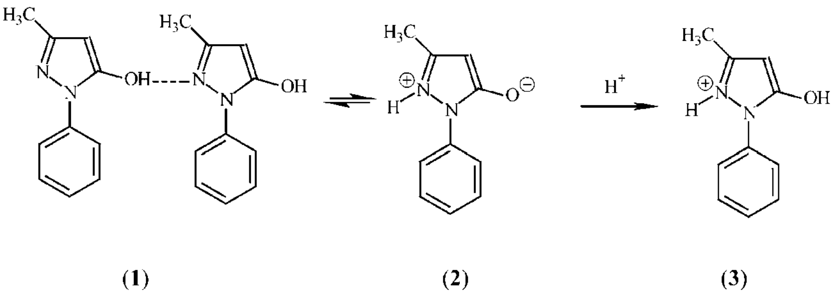


Figure 4. 4000–400 cm^{-1} IR spectra in solid state (KBr disks) of DPhP (1) and MPhP (2).



Scheme 3.

similar IR spectrum presents the protonated derivative of DPhP [Fig. 5, (1)]. However, in this case, another mechanism is at hand. The preliminary dissolution of the DPhP in methanol gives rise to the stabilization of the OH form (see above) and the consequent acidification of the imino nitrogen atom.

The calculated heats of formation, dipole moments, and single O and N atomic charges for the individual tautomeric CH and OH forms of both MPhP and DPhP in the gas phase are given in Table 1. The quantum chemical results elucidate the IR-spectral data stated above in the following way.

i. The calculations predicted an insignificant difference between the ΔH_f values of the CH- and OH-tautomers of the DPhP and MPhP, respectively. It should be noted that the CH-tautomeric form observed in nonpolar and low-polar solvents (see "Materials and Methods") do not correspond to the absolute ΔH_f data (Table 1). As in other pyrazol-5-one derivatives,[19,29,30] this indicates a very small role for intramolecular factors in the stabilization of their tautomeric structure.
ii. The carbonyl oxygen of both CH-tautomers possess the most negative charge, which is in agreement with favorable conversion to the OH form and explained the eventual processes (Scheme 2) in protic polar solvents, leading to the mentioned tautomeric rearrangement.
iii. The calculated larger permanent dipole moment of the CH-structure of both compounds can explain the preference for polar aprotic solvents. According to the reaction field approach, the polarity increase of the medium should favor a tautomer with greater dipole moment.[31]

All the conclusions above suggest the crucial importance of specific interactions such as intermolecular hydrogen bond formation on the OH-form stabilization. DPhP as well as MPhP exhibit this tautomer in protic (alcoholic) solutions; however, the situation is more specific in the solid state. The supramoleculr building of the methyl derivative is strongly reinforced by electrostatic interactions between the zwitterions that result from the corresponding OH form, but the solid-state DPhP is generated

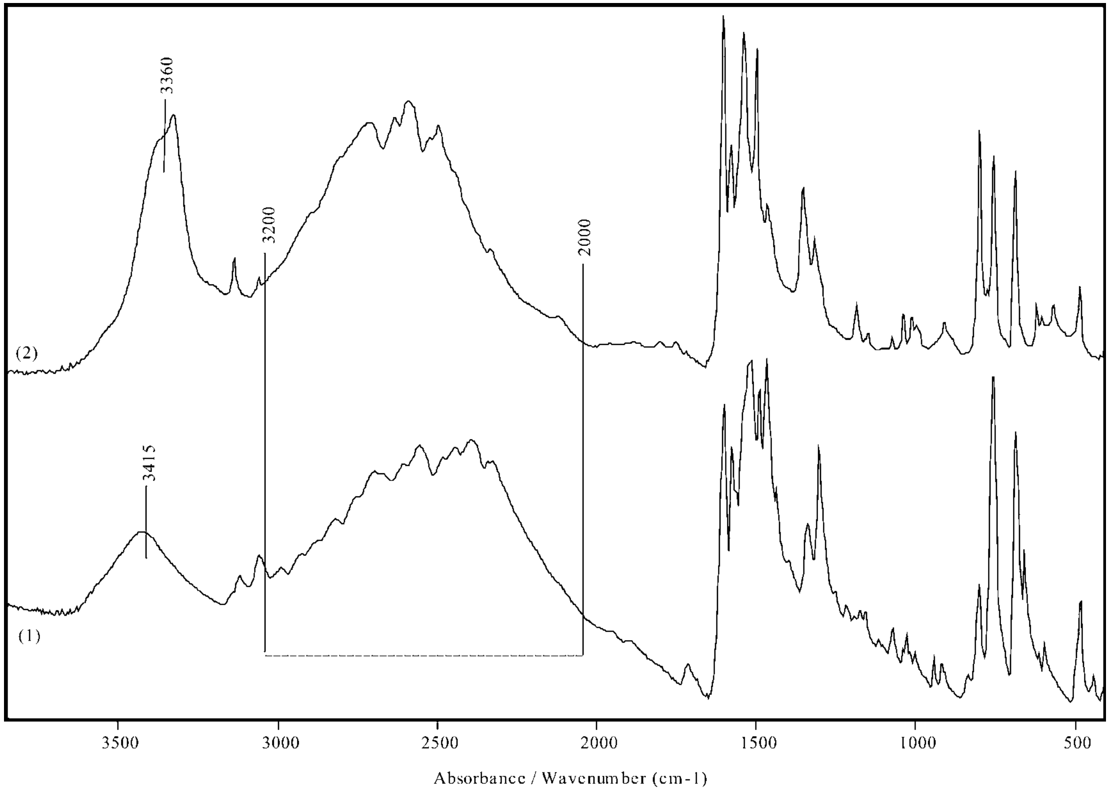


Figure 5. 4000–400 cm^{-1} solid-state IR spectra (KBr disks) of hydrochloric salts of DPhP (1) and MPhP (2).

from CH-tautomeric molecules. This structure is obtained after crystallization as from aprotic (carbon tetrachloride) as well as from protic (methanol) solvents. The quantum chemical results do not clarify the discussed phenomenon. Independently of the kind of the substituent at the 3-position, an almost equal charge distribution in the corresponding tautomers of both compounds is at hand. (Table 1). These apply also to the charge density of the imino-nitrogens, although DPhP could be affected because of the possible conjugation with the benzene ring. All these preconditions suggest a decisive importance of the steric repulsion caused by the bulky phenyl 3-substituent on the stabilization of the CH-structure of DPhP in the solid state.

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