

4-Methylquinolinium hydrogensquarate – crystal structure and spectroscopic elucidation

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4-Methylquinolinium hydrogensquarate (**1**) has been synthesized, and its structure and spectroscopic properties have been elucidated by means of single crystal X-ray diffraction, linear-polarized solid state IR-spectroscopy, UV-spectroscopy, ¹H-NMR, TGA, DSC, DTA and positive and negative ESI-MS. Quantum-chemical calculations were used to obtain the electronic structure, vibrational data and electronic spectrum of the target compound. The effects of N-protonation on the optical and magnetic properties were estimated by comparing the data of the protonated and neutral compound.

Keywords: 4-methylquinolinium hydrogensquarate, crystal structure, solid-state linear polarized IR-spectroscopy, UV-spectroscopy, quantum chemical calculations, ¹H-NMR.

INTRODUCTION

Quinolinium salts are a class of very important synthetic compounds. Similarly to other heteroarenium salts, they contain cyclic nitrogen atom with formal positive charge and lone electron pair bound to proton, alkyl, aryl or other organic fragments. Some representatives of this class are known to possess valuable physiological properties [1] such as anti-microbial, anti-tumor, hypotensive, ganglion-blocking ones, *etc.* Moreover, quinolinium salt fragments are included in the molecular structures of a number of polymethine dyes [2]. Certain quinolinium derivatives were found to act as plant growth regulators [3]. Recently, N-butyl-6-methylquinolinium salt was reported to be successfully applied as ionic liquid in dye-sensitized solar cells [4]. In another study, Engel *et al.* [5] have demonstrated generation of intramolecular photo-induced electron transfer in zwitterionic quinolinium salts, depending on the type of substituents, attached to the quinoline moiety. These interesting properties of the quinolinium salts, and previous publications in this field [6, 7] prompted

us to synthesize and explore the properties of 4-methylquinolinium hydrogensquarate as a potential material for the synthesis of new stilbazolium-type salts. The latter possess extended π -conjugated system with very large second-order nonlinear optical (NLO) susceptibilities. This has attracted a lot of scientific attention, due to the potential of the salts for use in electro-optic modulation [8], frequency conversion [9] and THz-wave generation and detection [10]. Todorova *et al.* have published structural and spectroscopic elucidation of a new stilbazolium dye with enlarged or conjugated system, which was synthesized by Knoevenagel-type condensation between 4-methylquinolinium iodide and the 4-dimethylaminonaphthaldehyde [11].

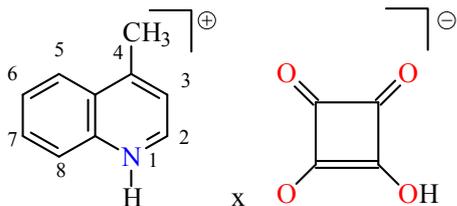
Squaric acid (H₂Sq) represents an attractive template for generating tightly hydrogen-bonded self-assemblies from polarizable cations in general, and basic amino acids in particular. During the last 15 years, series of non-centrosymmetric crystals were synthesized, isolated, and spectroscopically and structurally elucidated by means of single crystal X-ray diffraction studies. Squaric acid as a strong organic acid gives rise to stabilized hydrogensquarate (HSq⁻) anion and squarate dianion (Sq²⁻), which allows for the control of their self-assembly in crystals and for tuning their spectroscopic, optical and nonlinear-optical properties. New structural motifs of squaric acid derivatives of amino acids,

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amino acid amides and diamides were previously described by Kolev and co-workers [12–21] and other authors [22–30].

Therefore it seems important to expand the scope of these studies by elucidating the structural and spectroscopic properties of quinolinium salts of squaric acid. To this purpose, the target compound, 4-methylquinolinium hydrogensquarate was synthesized, according to Scheme 1, purified and further characterized. The present investigation is a continuation of systematic studies on the protonation and coordination capabilities of various substituted heterocycles [31–37]. Now we report the synthesis as well as the spectroscopic and structural elucidation of novel 4-methylquinolinium hydrogensquarate (**1**), both in solution and in solid-state by using single crystal X-ray diffraction, ¹H-NMR, positive and negative ESI mass spectrometry, UV-spectroscopy, conventional and linear polarized IR-spectroscopy, and the TGA and DSC. Quantum-chemical calculations at the DFT and MP2 levels of theory with the 6-31++G** basis set were employed for predicting and supporting the experimentally observed optical properties of the compounds studied. Regardless of the number of published studies on different substituted quinoline derivatives, crystallographic data, concerning 4-methylquinolinium salts are rare. Ten structures of cobalt, copper, ruthenium and osmium complexes [38–46] and only one structure of the salt have been reported so far such as 4-methylquinolinium chloro-trioxo-chromium(vi) complex [47].

The structure of 4-methylquinolinium hydrogensquarate is outlined below (Scheme 1):



Scheme 1. Chemical diagram of the 4-methylquinolinium hydrogensquarate (**1**).

EXPERIMENTAL

Methods

The *X-ray diffraction* intensities were measured in the ω scan mode on a Siemens P4 diffractometer equipped with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, $\theta_{\max} = 25^\circ$). The structure was resolved by direct methods and refined against F^2 [48, 49]. An *ORTEP*

plot illustrates the anion and cation moieties, *ADP* are at the 50% probability level. Relevant crystallographic data and refinement details are presented in Table 1. Both the conventional and polarized IR-spectra were measured on a Thermo Nicolet 6700 FTIR-spectrometer (4000–400 cm^{-1} , 2 cm^{-1} resolution, 200 scans). *Non-polarized solid-state IR spectra* were recorded using the KBr pellet technique. The oriented samples were obtained as a colloid suspension in a nematic liquid crystal ZLI 1695 (Merck, Germany). The theoretical approach, the experimental technique for preparing the samples, the procedures for polarized IR-spectra interpretation, and the validation of this new linear-dichroic infrared (IR-LD) orientation solid-state method for accuracy and precision have previously been published by Ivanova *et al.* [50]. The influence of the liquid crystal medium on the peak positions and integral absorbance of the guest molecule bands, the rheological model, the nature and balance of the forces in the nematic liquid crystal suspension system, and the morphology of the suspended particles were also discussed by Ivanova, *et al.* [50–53].

The *positive and negative ESI mass spectra* were recorded on a Fisons VG Autospec instrument. *Ultraviolet (UV-) spectra* were recorded on Tecan Safire Absorbance/Fluorescence XFluor 4 V 4.40 spectrophotometer operating between 190 and 900 nm, using acetonitrile as solvent (Uvasol, Merck) at a concentration of $2.5 \cdot 10^{-5} \text{ M}$, and 0.0921 cm^2 quartz cells.

Quantum chemical calculations were performed with GAUSSIAN 98 program packages [54]. The output files were visualized by means of the ChemCraft program [55]. The geometry of protonated form of the compound was optimized at two levels of theory: second-order Moller-Pleset perturbation theory (MP2) and density functional theory (DFT) using the 6-31++G** basis set. The DFT method employed is B3LYP, which combines Becke's three-parameter non-local exchange function with the correlation function of Lee, Yang and Parr. The absence of the imaginary frequencies as well as of negative eigenvalues of the second-derivative matrix confirmed that the stationary points correspond to minima of the potential energy hypersurfaces. The calculations of vibrational frequencies and infrared intensities were checked to establish which level of performed calculations are in good agreement with the obtained experimental data. The B3LYP/6-31++G** data were presented for above-discussed modes, where a modification of the results using the empirical scaling factors 0.9614 was made to achieve better correspondence between the experimental and theoretical values.

The *thermal analyses* were performed in the 300–500 K range on a Differential Scanning Calorimeter

Table 1. Crystal and refinement data for (1)

Empirical formula	C ₁₄ H ₁₁ NO ₄	
Formula weight	257.24	
Temperature (K)	293(2)	
Wavelength (Å)	0.71073	
Crystal system, space group	Triclinic, P $\bar{1}$	
Unit cell dimensions	$a = 8.0666(16)\text{Å}$	$\alpha = 87.97(3)^\circ$
	$b = 8.5919(17)\text{Å}$	$\beta = 77.46(3)^\circ$
	$c = 9.7079(19)\text{Å}$	$\gamma = 66.34(3)^\circ$
Volume (Å ³)	600.6(2)	
Z	2	
Calculated density (Mg·m ⁻³)	1.423	
Absorption coefficient (mm ⁻¹)	0.106	
F(000)	268	
Crystal size (mm)	0.45 × 0.43 × 0.38	
θ range for data collection	2.15 ≤ θ ≤ 25.27	
<i>hkl</i> indices	0 ≤ <i>h</i> ≤ 6, -8 ≤ <i>k</i> ≤ 10, -11 ≤ <i>l</i> ≤ 11	
Reflections collected / unique	1875/1716, R(int) = 0.0468	
Absorption correction	multi-scan	
Goodness-of-fit on F ²	1.022	
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0696, wR2 = 0.1525	
R indices (all data)	R1 = 0.1618, wR2 = 0.1977	
max./min. res. (e·Å ⁻³)	0.221/ -0.280	

Perkin-Elmer DSC-7, and a Differential Thermal Analyzer DTA/TG (Seiko Instrument, model TG/DTA 300). The *elemental analysis* was carried out according to the standard procedures for C and H (as CO₂, and H₂O) and N (by the Dumas method).

Synthesis

4-Methylquinolinium hydrogensquarate (1) was synthesized by the following procedure: Squaric acid 342 mg (3 mmol) was dissolved in 50 ml distilled water. 435 mg of 4-methylquinoline (3 mmol) dissolved in 10 ml methanol were added dropwise to the aqueous solution by continuous stirring at room temperature for 6 h. After complete dissolution, the reaction mixture was set aside to crystallize for two weeks. The product was then purified by multiple recrystallizations from distilled water, and was finally obtained in 85% yield. Crystals suitable for X-ray diffraction studies were grown by slow evaporation from a mixture of water- methanol (1:1 v/v). After several weeks, colorless crystals were isolated, filtered and dried at room temperature. (Found: C, 65.4; H, 4.3; N, 5.4; [C₁₄H₁₁NO₄] calcd.: C, 65.4; H, 4.3; N, 5.40%). The strongest signal in the positive ESI mass spectrum corresponded to the peak at *m/z* 144.62 which represents singly-charged cation [C₁₀H₁₀N]⁺ with a molecular weight of 144.20. The

TGA and DSC data recorded within the temperature range of 300–500 K showed that solvent molecules were not incorporated in the crystal structure of the target compound.

RESULTS AND DISCUSSION

Crystal structure of (1) and molecular geometry of the 4-methylquinolinium cation

Compound (1) crystallizes in the centrosymmetric space group P $\bar{1}$. The ORTEP diagram of the asymmetric unit is given in Fig. 1. The structure consists of infinite layers (Fig. 2), formed by means of intermolecular N⁺H...O=C_(sq) hydrogen bonds of length 2.752 Å between the cations and anions. The hydrogensquarate moieties form stable dimers, which is a typical structural motif in the crystals with differently substituted pyridinium counter ions [34–36] *via* strong hydrogen _(sq)OH...O=C_(sq) bonds (2.595 Å) (Fig. 2). In the unit cell, the two cations are disposed in a co-planar manner (Fig. 2), thus leading to a co-linear orientation of the out-of-plane (*o.p.*) normal modes of the quinoline-fragment (see below). The cation is effectively flat with a dihedral angle between the planes of the fused aromatic rings of only 0.8(2)°. The geometrical parameters of

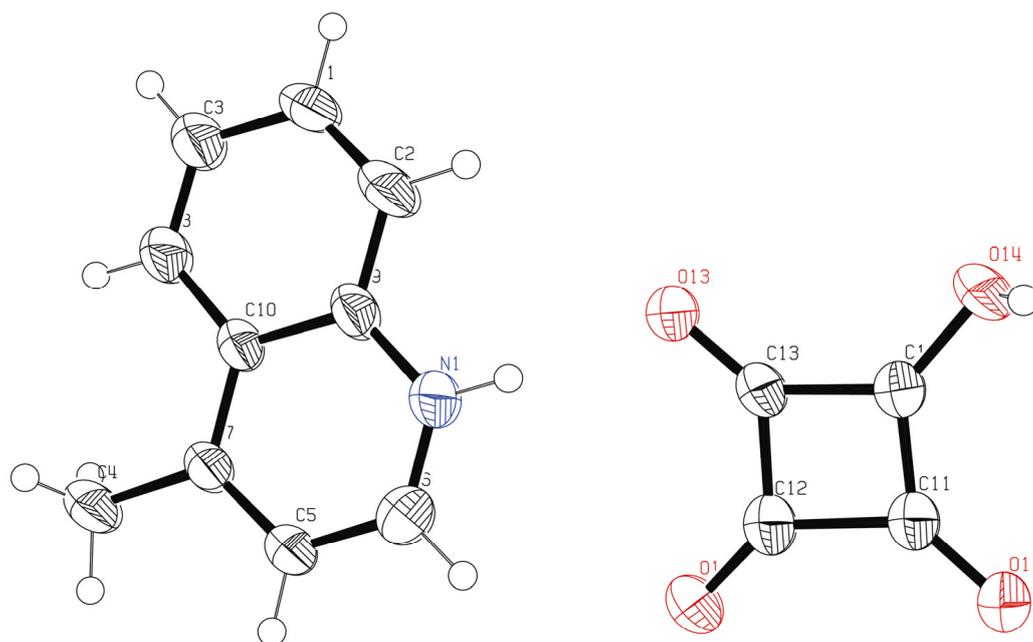


Fig. 1. The molecular structure of (1). Displacement ellipsoids are drawn at the 50% probability level.

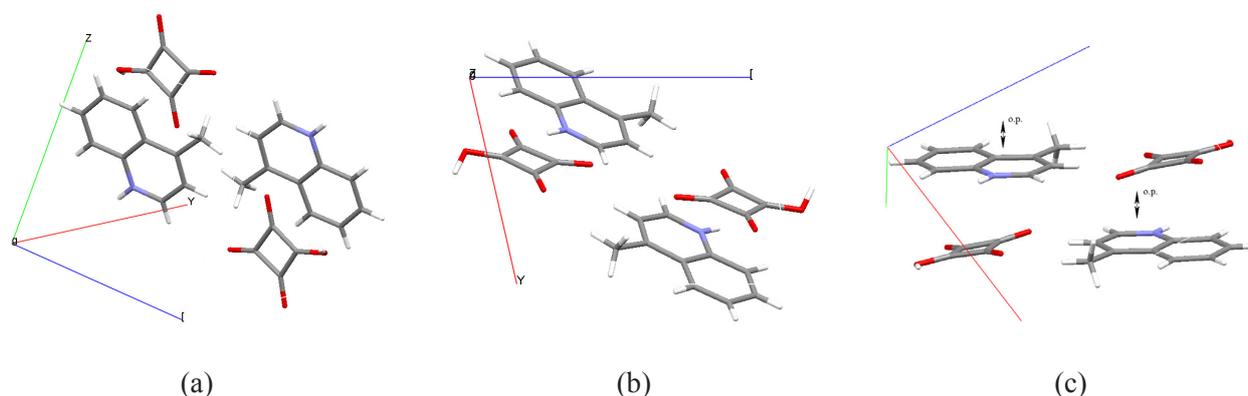


Fig. 2. Unit cell (a), view along *b*-axis (b) and visualization of the direction of the out-of-plane normal modes (c) of the 4-methylquinoline fragment obtained by group analysis.

the cationic moiety lie within the range of the previously reported salt [47].

The calculated electronic structure of the protonated 4-methylquinoline correlated well with the experimentally obtained structure. The calculations at the approximation used generated a structure (Fig. 3), with geometry parameters differing from the experimental values by maximum values of 0.021 Å and 1.6(3)°. Therefore, a very good coincidence between the experimental and calculated values exists.

Electronic spectra

The UV-vis spectrum of (1) in acetonitrile is depicted in Fig. 4. According to literature data, the electronic spectrum of the neutral form is characterized by three bands within the 265–275 nm, 300–305 nm and 310–315 nm ranges, depending on the solvent type. The corresponding ϵ -values were, approximately, 4000, 2300 and 2100 l.mol⁻¹.cm⁻¹, respectively [57]. The effect of protonation led to a hypsochromic shift of the discussed maxima.

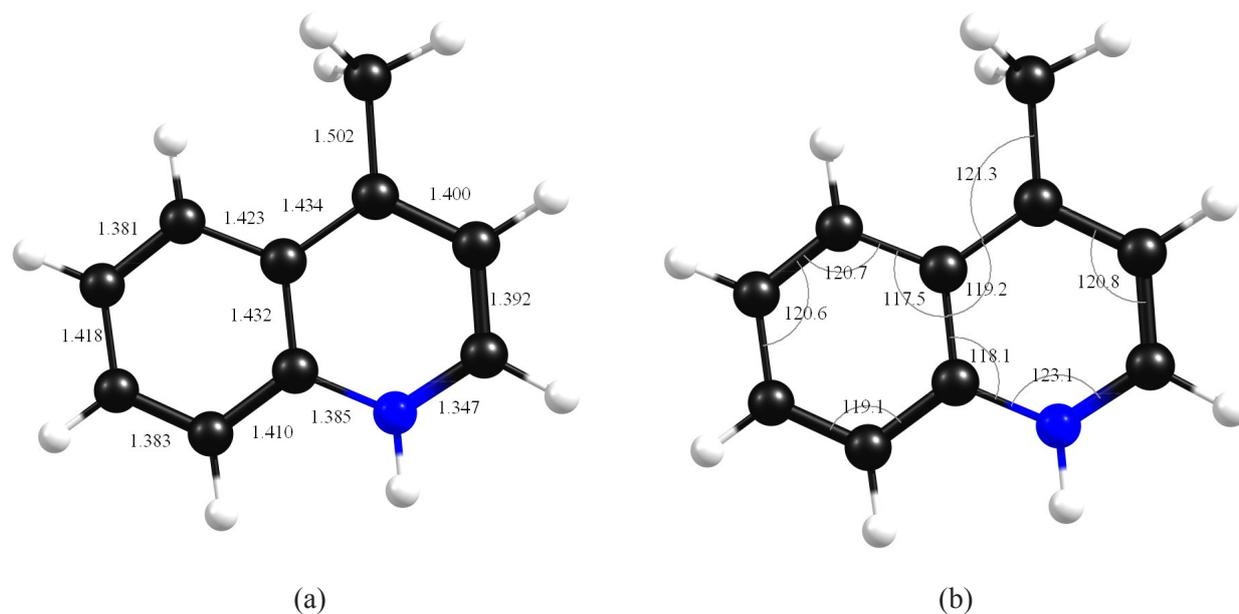


Fig. 3. Predicted geometry parameters of protonated 4-methylquinoline, the bond lengths are given in [Å] (a), bond angles in [°] (b), respectively.

The corresponding values amounted to 238 nm ($\epsilon = 4467 \text{ l.mol}^{-1}.\text{cm}^{-1}$), 254 nm ($\epsilon = 2231 \text{ l.mol}^{-1}.\text{cm}^{-1}$) and 277 nm ($\epsilon = 2000 \text{ l.mol}^{-1}.\text{cm}^{-1}$). The low intensity bands at about 310 nm with ϵ value of $1000 \text{ l.mol}^{-1}.\text{cm}^{-1}$ corresponds to hydrogensquarate species.

The experimentally observed data correlate well with the theoretically predicted electronic spectra of protonated 4-methylquinoline. The observed

absorption bands were 235 nm (coefficient of the probability of the transition, $f = 0.0330$), 260 nm ($f = 0.0610$) and 280 nm ($f = 0.0098$), respectively. The differences between the theoretically predicted and experimentally observed data obtained were less than 5 nm. These results suggest that the N-protonation leads to a partial charge re-distribution within the 4-methylquinoline molecule (Fig. 4).

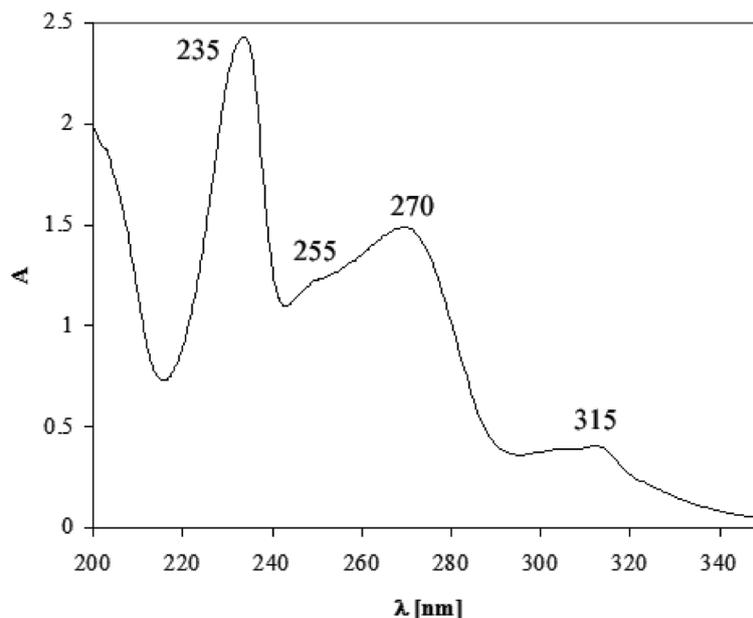


Fig. 4. UV-Vis spectrum of (1) in acetonitrile at concentration $2.5 \cdot 10^{-4} \text{ mol/l}$.

The theoretical data indicate that the structural shift is predominantly localized in the conjugated plane and that the groups, not belonging to the conjugated plane do not change significantly (Fig. 5).

IR-spectroscopic data

The IR-spectroscopic elucidation of (**1**) was performed by comparing the experimental IR-char-

acteristics (Fig. 6) with the corresponding theoretical vibrations of protonated 4-methylquinoline (Fig. 7).

The experimental IR-spectrum of (**1**) was characterized by a broad absorption band within the 3000–1900 cm^{-1} region, corresponding to overlapped $\nu_{\text{OH(Sq)}}$ and $\nu_{\text{N+H}}$ stretching vibrations (Fig. 6). The last vibration was theoretically predicted at 3576 cm^{-1} (Fig. 7), but the participation of the N^+H group in intermolecular hydrogen bonding leads

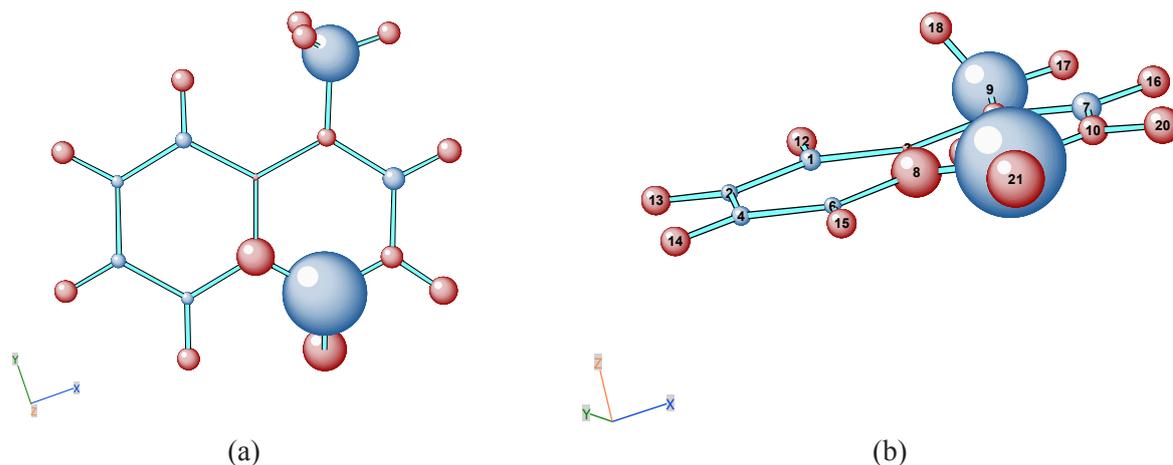


Fig. 5. Theoretical predicted single atomic charges of protonated 4-methylquinoline (a) and another view (b). The sizes of the spheres are proportional to charges on atoms.

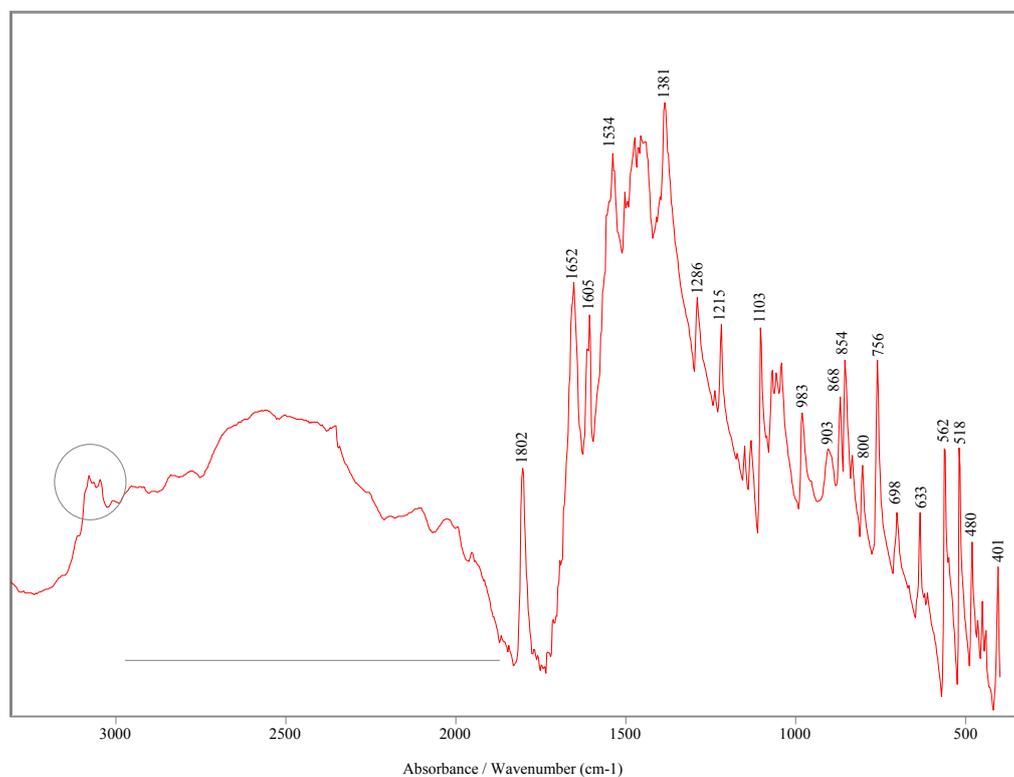


Fig. 6. IR-spectrum of (**1**) in KBr pellet.

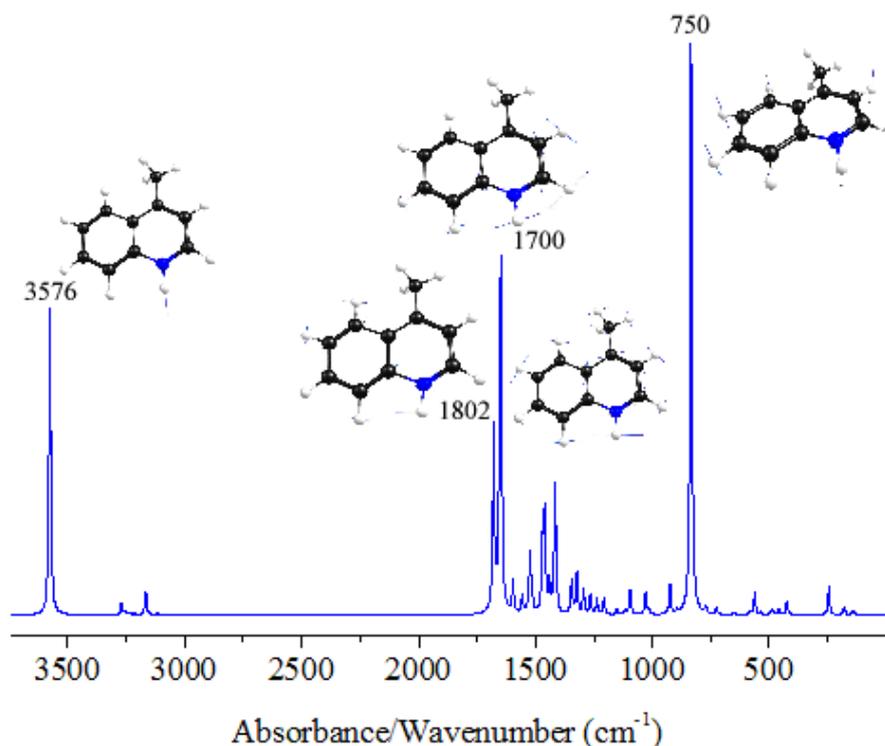


Fig. 7. Theoretical IR-spectrum of protonated 4-methylquinoline and visualization of selected directions of the molecular motion.

to a significant low-frequency shifting. The series of bands within the 3100–3000 cm^{-1} region corresponds to in-plane (*i.p.*) stretching vibrations ν_{ArH} in both the theoretical and experimental IR-spectra. The bands at 1802, 1700 and 1534 cm^{-1} belong to $\nu_{\text{C=O(Sq)}^{\text{s}}}$, $\nu_{\text{C=O(Sq)}^{\text{as}}}$ and $\nu_{\text{C=C(Sq)}}$ stretching vibrations of the hydrogensquarate anion, respectively (Fig. 6). The bands at 1652 cm^{-1} and 1605 cm^{-1} could be attributed to $\delta_{\text{N+H}}$ bending vibrations and *i.p.* vibrations of the quinoline fragment (Fig. 7). The corresponding theoretical values are 1633 cm^{-1} and 1604 cm^{-1} , respectively. The high-frequency shift of $\delta_{\text{N+H}}$ results from intermolecular interactions in the solid-state, and the obtained difference of 19 cm^{-1} for the first IR-band is therefore expected. The IR-spectrum of (1) is characterized by strong band at 1381 cm^{-1} , belonging to *i.p.* vibrations of quinoline fragment (theoretical value of 1380 cm^{-1}). The other IR-bands observed within the 1300–950 cm^{-1} range also belonged to the *i.p.* vibrations of the latter fragment. The broad band at 903 cm^{-1} (Fig. 6) could be assigned to the $\gamma_{\text{N+H}}$ mode (theoretical value of 750 cm^{-1}). Similarly to $\delta_{\text{N+H}}$, the participation of the $\text{N}^{\text{+}}\text{H}$ group in the intermolecular interactions leads to a high-frequency shift of the $\gamma_{\text{N+H}}$ IR-band as well.

The bands at 869, 854 and 833 cm^{-1} (theoretical values of 870, 855 and 833 cm^{-1} , respectively) belong to the out of-plane (*o.p.*) bending vibrations

of the 4-lepidine fragment. A direct experimental confirmation of their assignment follows from the obtained elimination of these maxima at an equal dichroic ratio (Fig. 8). Regardless of this observation, the discussed IR-bands are split into pairs as a result of the crystal field splitting in the case of $Z = 2$. Total disappearance of the maxima during the elimination procedure was observed. At the same time, disappearance of the band at 903 cm^{-1} was also found (Fig. 8), which was in accordance with the geometry obtained, since the normal modes of the *o.p.* and $\gamma_{\text{N+H}}$ modes are oriented in a mutually co-linear manner.

Hence the vibrational assignment of the bands belonging to structure (1) was made on the basis of calculated IR frequencies, and their intensities were supported by the polarization IR spectral data. The coincidence between calculated and measured frequencies was found to be satisfactory.

^1H - and ^{13}C -NMR data

According to literature data, the chemical shift signals of the C2H, C3H, C5H–C7H (Scheme 1) in the ^1H NMR spectrum of the neutral molecule 4-methylquinoline are observed at about 8.77, 7.21, 7.98, 7.55, 7.70 and 8.10 ppm, while the signal of $-\text{CH}_3$ is at 2.79 ppm [57, 58]. The effect of

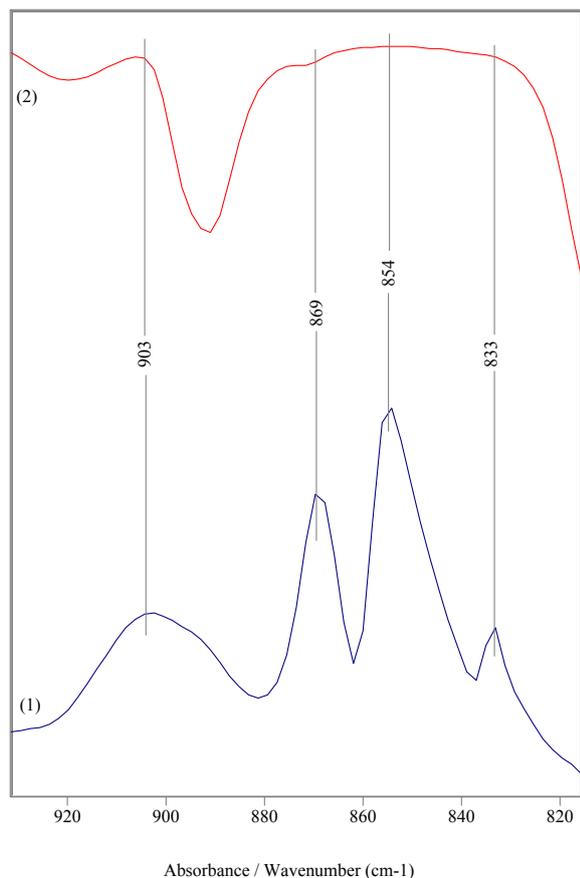


Fig. 8. Non-polarized IR-(1) and reduced IR-LD (2) spectra of (1) after elimination of the band at 854 cm^{-1} .

N-protonation leads to a downfield shifting of the signals of C2H and C3H by about 0.5–0.7 ppm.

CONCLUSIONS

The new compound, 4-methylquinolinium hydrogensquarate has been synthesized, isolated, and spectroscopically and structurally elucidated by using single crystal X-ray diffraction, IR-LD spectroscopy, UV-spectroscopy, $^1\text{H-NMR}$, thermal methods and mass spectrometry. Quantum chemical calculations are used to obtain the electronic structure, vibrational data and electronic spectra. The effects of N-protonation on the optical and magnetic properties are elucidated by comparing the data of the protonated and neutral compound. Compound crystallizes in the centrosymmetric space group $P\bar{1}$, and the structure consists of infinite layers, formed by intermolecular $\text{N}^+\text{H}\dots\text{O}=\text{C}_{(\text{sq})}$ hydrogen bonds (2.752 Å) between the cations and anions. The hydrogensquarate moieties form stable dimers by

means of strong hydrogen ($_{(\text{sq})}\text{OH}\dots\text{O}=\text{C}_{(\text{sq})}$) bond (2.595 Å). The two cations are found to be in coplanar arrangement within the unit cell, thus indicating a successful application of the reducing-difference-procedure for polarized IR-LD spectra interpretation. Moreover, the N-protonation leads to a partial charge redistribution of the protonated 4-lepidine.

SUPPORTING INFORMATION

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC 705630. Copies of this information can be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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4-МЕТИЛХИНОЛИНИЕВ ХИДРОГЕНСКВАРАТ: КРИСТАЛНА СТРУКТУРА И СПЕКТРАЛНА ОЦЕНКА

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(Резюме)

Синтезирано е съединението 4-метилхинолиниев хидрогенскварат и са определени неговата структура и спектрални характеристики чрез инструментални методи, като монокристален рентгеноструктурен анализ, линейно поляризирана инфрачервена спектроскопия в твърдо състояние, UV-спектроскопия, ¹H-NMR, TGA, DSC, DTA и ESI-MS. Използвани са квантово-химични изчислителни процедури, за да се генерират електронната структура, както и теоретични спектрални данни за изследваното съединение. Влиянието на протонирането при азотния атом върху оптичните и магнитни свойства е оценено чрез сравняване на съответните данни за протонираната и непротонирана форма на 4-метилхинолиниев хидрогенскварат.