

Contents lists available at ScienceDirect

Journal of Molecular Structure





Cetylpyridinium picrate: Spectroscopy, conductivity and DFT investigation of the structure of a new ionic liquid



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ARTICLE INFO

Article history: Received 19 October 2020 Revised 12 November 2020 Accepted 19 December 2020 Available online 24 December 2020

Keywords: Cetylpyridinium Charge transfer Conductometry DFT NMR XRD

ABSTRACT

A new cetylpyridinium picrate ionic liquid has been synthesized and characterized by differential thermal analysis, XRD, FT-IR, and NMR (¹H and ¹³C) spectroscopy. Differential thermal analysis indicates the congruent melting of cetylpyridinium picrate and a temperature range of liquid state is 47–267 °C. A solid form of the sample characterized with a polymorphic transformation at 37 °C, which was confirmed via the XRD analysis.

The interionic charge-transfer interactions, namely the charge transfer from the picrate anion to the cetylpyridinium cation, were detected by comparison of NMR spectra of DMSO solutions of the ionic liquid and cetylpyridinium chloride. The H–NMR chemical shifts' differences of about 0.2 ppm and 0.1 ppm were observed in the case of the *o*-protons and the α -methylene group protons, respectively. Additionally, the charge-transfering between the attracted ions was confirmed by DFT calculations.

Based on the solid state NMR technique, the higher ions mobility was suggested for the solid sample of the ionic liquid in comparison to the solid cetylpyridinium chloride monohydrate. Moreover, the association constants K_A at 22, 30, 40, and 50 °C, obtained from the electrical conductivity measurements, clearly testifies much lower dissociation in the case of picrate. The K_A values of cetylpyridinium picrate and chloride in DMSO medium at 22 °C equal 748.7 L/mol and 525.0 L/mol, respectively.

The performed DFT computations of the reduced density gradient function in four proposed structures of the new ionic liquid cation-anion pair identifies the presence of weak non-covalent $C-H\bullet\bullet O=N$ interactions between cetyl chain hydrogen atoms and nitro groups of picrate was explored through DFT calculations and analysis of the RDG function.

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1. Introduction

Cetylpyridinium (CP) cation, also called 1-hexadecylpyridinium, has been a steady focus of scientific interest. According to the Google Scholar database, "hexadecylpyridinium" was mentioned in 2560 and "cetylpyridinium" in 15,300 publications and patents in the period 2010–2019.

The scientific interest in the CP cation is motivated by the extensive usage of its salts in industrial and commercial cleaning formulations, cosmetics, and pharmaceuticals. The use of CP salts mainly due to its antiseptic [1–3] and surfactant [4–8] properties, while some are used as catalysts in organic synthesis [9]. The most common commercially available salts of CP are chloride (CPC) and bromide, in monohydrate or anhydrous forms. The CP cation is also very popular in the field of analytical chemistry, primarily for its cationic surfactant nature and ability to act as a counter-ion in ion-pair based ionophores. CP cations have been used for the construction of ion-selective electrodes' membranes sensitive to iodide [10], periodate [11], and alkyl sulfates [12], and can be used for the detection of cholesterol [13]. Moreover, CP can be used to modify silica to improve the analysis of food dyes [14].

Taking into account the wide usage of CP-containing compounds and the longstanding interest in CP-selective membranes, we investigated the CP dipicrylamide ionic pair as an ionexchanger for a plasticized CP-selective electrode in a previous work [15]. Continuing our investigations in this field, we have synthesized cetylpyridinium picrate (CPPA). The CPPA ionic pair has a low melting point (47 °C), and can be considered a lowtemperature ionic liquid [16]. It must be noted that the formation of the CPPA ion pair has been studied previously [17] and this as-

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sociation process in water can be used for the detection of CPC [18].

Taking a step aside from analytical measurements and applications, we decided to explore the molecular and electronic structure of this compound with the assumption that such knowledge will support the explanation and interpretation of future studies of its role as an ion-exchange agent. Thus, in the present work, we discuss the structure of the ionic liquid that consists of the CP cation and the picrate anion (PA) – CPPA.

Ionic liquids (ILs) form a wide class of organic salts that have relatively low melting temperatures (below 100 °C) and remain liquid across a wide temperature range [19,20]. ILs' crystal structures are responsible for their low melting points; they are generally built from large, asymmetric organic cations and organic/inorganic anions bonded together by weak van der Waals or hydrogen bonds to form a dimensional framework [19,21,22]. These structures determine their interesting physico-chemical properties, like high electrical conductivity and thermal stability [23], good solvating characteristics, negligible vapor pressure, and high viscosity [19,21,24,25].

The large number of available bulky organic ions and their many possible combinations enable wide variability in the composition of ILs and their adjustment to meet the requirements of a particular process (as "designer solvents"). Due to the wide variability of ILs and the possibility of tuning their composition and properties, ILs have found application as novel solvents in organic synthesis [26], for separation in analytical chemistry [27], and as solvents for nanoparticles stabilization [28] in addition to serving as catalysts [29], corrosion inhibitors [30], lubricants [31], and electrochemical sensors and electrolytes [32]. ILs also exhibit biological activity and can be used in pharmaceuticals [33].

2. Experimental

2.1. Synthesis of cetylpyridinium picrate (CPPA)

Caution! Synthesis must be executed with specific safety precautions. Picric acid is explosive and corrosive. CPC is irritating to skin and eyes and toxic if swallowed or inhaled. Distillated water was used in all experiments.

Picric acid (2.30 g, 10 mmol) was dissolved in 50 mL of water with NaOH (0.41 g, 10 mmol) to obtain clear yellow solution A. CPC monohydrate (3.58 g, 10 mmol) was dissolved in 100 mL of warm water (solution **B**). Solutions **A** and **B** were mixed with the immediate formation of bright yellow oil. The yellow oil solidified upon standing at room temperature for 2 days. The precipitate was filtered, washed with water, and air-dried. The result was a yellow solid in 92% yield (4.90 g), mp 46 °C. ¹H NMR (DMSO d_{6} , 400 MHz), δ (ppm): 9.08 (2H, d, o-CH_{pyridinium}), 8.60 (1H, t, p-CH_{pyridinium}), 8.58 (2H, s, CH_{picrate}), 8.15 (1H, t, *m*-CH_{pyridinium}), 4.58 (2H, t, CH₂N), 1.90 (2H, m, β -CH₂), 1.22–1.26 (26H, m, 13[CH₂]), 0.84 (3H, t, CH₃). ¹³C NMR (DMSO, 100 MHz), δ (ppm): 160.80, 145.43, 144.71, 141.83, 128.06, 125.15, 124.10, 60.78, 31.28, 30.71, 29.03, 29.00, 28.90, 28.76, 28.69, 28.36, 25.39, 22.07, 13.89. Elemental analysis, found (%): C, 61.1; H, 7.8; N, 10.3; molecular formula C₃₃H₄₂N₈O₁₂ requires (%): C, 60.9; H, 7.6; N, 10.5.

2.2. Instruments and measurements

Fourier-transform infrared spectra (FT-IR) were recorded on a Shimadzu IRPrestige-21 spectrometer in attenuated total reflection (ATR) mode with a zinc selenide crystal.

NMR spectra of CPPA and CPC solutions in deuterated dimethyl sulfoxide (DMSO-d6) were recorded on a Varian Mercury-400 instrument with tetramethylsilane used as an internal standard.

DMSO-d6 solutions of CPPA and CPC were obtained by dissolving of 49 mg and 33 mg of salts in 0.6 mL of the solvent, respectively.

Solid-state NMR spectra of CPPA and CPC were recorded on a Varian 400 MHz NMR spectrometer using adamantane as an external standard. The MAS frequency used for the measuring of ¹H NMR spectra was 12 kHz. ¹³C NMR spectra were acquired using cross-polarization, dipolar decoupling (DD), and magic angle spinning (MAS) with a spinning rate of 10 kHz.

The XRD powder patterns of CPPA samples were recorded using an AXRD Benchtop powder diffractometer (Proto Manufacturing Limited) equipped with a hybrid photon counting detector. The experimental data were collected in the $\theta/2\theta$ mode (Bragg–Brentano geometry) using the CuK α radiation (Ni filter) in 5–70 2θ angle range with 0.02° step, counting time of 1 s per step and a dynamic region of interest. Lattice constants were determined using Expo2014 software [34]. PowderCell 2.4 [35] was used for phase analysis.

The CPPA samples were characterized using differential thermal analysis (DTA). The DTA curves of CPPA were recorded in the air atmosphere in the temperature range 25–400 °C with a heating rate of 12 °C/min. The temperature of the effects on the DTA curves was determined as proposed in [36].

Conductometric studies were carried out with a WTW inoLab Multi 9620 IDS digital conductivity meter. The specific conductance (κ) of CPPA and CPC monohydrate in DMSO was measured for the temperature range from 22 to 50 °C. The temperature of solutions was maintained with an accuracy of ±0.1 °C using the LabExpert 1021 water thermostat.

2.3. Computational software and methods

The starting geometries were created and pre-optimized in Avogadro [37]. Refinements of the geometries of considered CPPA structures were performed with PBE GGA functional [38] and 6– 311G(d,p) basis sets [39]. The selection of this method was motivated by the good performance of GGA functionals with triple-zeta basis sets for modeling of geometric parameters of ionic liquids [40,41] and by our previous good experience in using the PBE/6– 311G(d,p) combination [42–44]. All computations related to PBE functional were done using PRIRODA 19 code [45].

The computations related to PBE0 [46], M06–2X [47] and ω B97X [48] functionals were performed in the ORCA 4.2.1 package [49]. The investigation of non-covalent interactions (NCI) with reduced-density-gradient (RDG) method [50] and related atoms-in-molecules (AIM) analysis of critical points were performed with Multiwfn 3.6 [51]. In the present study, different atomic population analyses were performed to obtain partial atomic charges: Mulliken, atomic dipole moment corrected Hirshfeld (ADCH) [52] scheme, and natural population analysis (NPA). NPA was performed with JANPA 2.01 [53]. Gabedit [54] was used for input file preparation, and VMD [55] for visualization.

3. Results and discussion

3.1. Structure of the cetylpyridinium picrate ionic liquid

The CPPA ion pair was obtained as a product of an ion-exchange reaction between CPC and PA in water (Scheme 1). An equimolar amount of NaOH was used for the neutralization of picric acid. This step also prevents possible hydrogen chloride formation from the reaction of CPC with picric acid and shifts the reaction equilibrium to the formation of the desired CPPA. The association of the PA and CP cation is driven by the electrostatic attraction between the negatively charged phenolic oxygen of the PA and the positively charged nitrogen of the pyridinium ring. However, literature data testify that interactions of PA with organic cations in ionic liquids



Scheme 1. Synthesis of CPPA ionic liquid.

Table 1

Relative total energies (E), enthalpies (H) and Gibbs free energies (G) (in kcal/mol) of forms **A–D** computed with three different functionals; the number of non-covalent BCPs between anion and cation in CPPA (N_{BCPs}); the maximal value of BPC's electron density (MAX_{BCP}, $e \times Å^{-3}$); the sum of electron density values of all interionic BPCs ($\Sigma \rho(r)_{BCP}$, $e \times Å^{-3}$).

	PBE-D3BJ		PBE0-D3BJ		M06-2X							
PBE0-D3BJ	E	Н	G	E	Н	G	E	Н	G	N _{BPCs}	$\Sigma \rho(\mathbf{r})_{BCP}$	MAX _{BCP}
Α	2.12	2.12	1.43	3.27	3.28	2.58	2.53	2.54	1.84	6	0.410	0.136
В	2.09	2.00	2.05	3.59	3.50	3.54	3.45	3.36	3.41	7	0.444	0.150
С	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7	0.621	0.226
D	2.41	2.39	1.35	3.06	3.05	2.01	1.89	1.87	0.83	4	0.295	0.123

have a complex character, and numerous $N=O\cdots H-C$ interactions are present [56].

To explore the anion-cation interactions in the synthesized ionic liquid, we analyzed the electronic structure of the CPPA molecule using DFT. Numerous works on organic ionic pairs [15,40,57] have shown that different optimized relative positions of ions cause only marginal energy differences among the corresponding structures; consequently, numerous different geometries can exist in equilibrium. In the present work, we have adopted an established known methodology for modeling pyridinium-based ionic associates [40]. We have considered four cation-anion dispositions, where the anion is placed in the inside and outside cavities formed by two rotamers of CP, one with the perpendicular arrangement of the cetyl chain with the pyridinium ring, and the other almost linear cation (see Fig. 1). PA can interact with the CP cation in different ways. That is why, in all structures considered, we have imposed anion such that the phenolic oxygen was as close as possible to the o-position of the pyridinium and the α -methylene group of the cetyl chain, as these are the most positively charged areas of the CP cation [15]. Optimization of molecular geometries and calculations of corresponding Hessians, zeropoint vibrational energies and entropies were performed at the PBE/6-311G(d,p) level.

During the geometry optimization of structure C, the anion shifted from the cavity significantly and coordinated near the side of the pyridinium cycle. In the resulting geometry, both the anion and the cation rings were nearly in one plane. Cartesian atomic coordinates of optimized geometries are presented in the supplementary materials.

Table 1 shows the relative total energies, enthalpies, and Gibbs free energies of all four possible structures **A–D**. Single point calculations of total energies with PBE, PBE0, M06–2X functionals in combination with the 6–311G(d,p) basis set were performed on the geometries optimized at the PBE/6–311G(d,p) level. According to the data in Table 1, the arrangement **C** is for 0.83–3.59 kcal/mol more stable than the other considered structures. This stabilization can be explained by the formation of multiple non-covalent interactions between the anion and the alkyl chain and the ring of the cation. It is possible that multiple forms exist in the real bulk ionic liquid sample, and some kind of agglomerates may even be preferable. However, at this point, consideration of the simplified forms **A–D** gives a general idea of the different anion–cation interactions.

Analysis of structures A-D in terms of atoms-in-molecules theory shows the presence of several interionic bond critical points (BCP) (purple dots in Fig. 1). The number of these non-covalent BCPs is 4 in **D**, 6 in **A**, and 7 in **B** and **C** (Table 1). In the case of structures **A**, **B**, and **D**, N=O•••C and N=O•••H–C interactions are present, whereas in structure **C**, only N=O•••H–C interionic interactions were detected. Moreover, in geometry **C**, four BCPs correspond to the anion–alkyl chain interactions, unlike **A**, **B**, and **D**, where the anion–cetyl chain interactions are characterized by only two BCPs. The correlation between the **A–D** forms' total enthalpies and maximal electron density of interionic BCP, or the sum of electron densities of interionic BCPs, is presented in supplementary materials. The sum of characteristic values of non-covalent BCPs was used as for the explanation of ion association in our previous study [42].

Visual analysis of the nature of non-covalent interactions (NCI) can be done using the reduced density gradient (RDG) method [50]. A visualization of this analysis for structures A-D is shown in Fig. 1. Red localized areas inside the rings correspond to the steric repulsive interactions, whereas the large green areas represents van der Waals interactions in the CPPA associate. Blue areas correspond to H-bonds (strong interaction). This analysis explains the stability of structure **C**; a strong interaction is present between the phenolic oxygen of PA and the *o*-hydrogen of the pyridinium ring. The scatter graphs of the RDG analysis presented in supplementary materials.

AIM analysis of BCPs and NCI explored via the RDG function indicate the presence of numerous weak interactions between the CP cation and the PA. Many weak van der Waals interactions are due to the N=O•••H-C attraction between anion and cation. The analysis of the anion's electron density generated at the PBE/6-311G(d,p) level, identifies the partial negative charge of the nitro groups. Hence, Mulliken, ADCH, and NPA partial charges and the Mayer bond order analysis indicate high charge delocalization, which can be explained by the presence of numerous resonance forms (see Scheme 2). The choice of ADCH partial charges was dictated by the known excellent performance of these charges for the reproduction of molecular dipole moments and chemical reactivity [58], in contrast to Mulliken and natural partial atomic charges, which are useful in the prediction of physical properties (e.g. $logP_{olw}$) [59].

In Mulliken population analysis, the partial charge of phenolic oxygen equals -0.28e, and the charges of oxygen atoms of the nitro groups are in the range-0.25e to -0.29e. Similar electron density redistribution is observed for the ADCH (NPA) population scheme: the partial charge of the phenolic oxygen is -0.37e (-0.54e) and the partial charges of the nitro group oxygen atoms are in the range-0.29 to -0.32e (from -0.35 to -0.42). The bond order



Fig. 1. Four structures represent the different reciprocal arrangement of CP and PA ions in the CPPA ionic associate: (A) CP rotamer is linear and PA coordinated outside the cavity; (B) CP cation is linear and PA located inside the cavity; (C) the cetyl chain is perpendicular to the pyridinium ring, and the anion is inside the cavity; (D) the same structure as C, but with the anion outside the cavity. The non-covalent bond critical points are shown as purple dots and the corresponding paths are shown as yellow lines. Reduced density gradient isosurface plot for four different anion-cation arrangements. The strong H-bond in structure C is shown.



Scheme 2. Resonance structures of PA.



Fig. 2. DTA curve of CPC monohydrate (A), as-synthesized CPPA after first and second heating (B) and DTA curves of once-melted CPPA (C).

analysis indicates the presence of a double bond between the phenolic oxygen and the ring, which is in agreement with the literature [60]. The nitrogen-oxygen bond orders are close to 1.5, whereas the C-NO₂ bonds are single, with orders of about 0.8– 0.9. The four analyses indicate that the formal negative charge was nearly equally delocalized over all oxygen atoms of the PA. The full list of the partial charges and bond orders is provided in the supplementary material.

3.2. Differential thermal analysis

DTA analysis was used to establish the melting point and the decomposition temperature of CPPA. The DTA heating curve of CPPA was compared with the heating curves of CPC and PA to confirm the absence of CPC and picric acid impurities. PA melts at 117 °C and begins to decompose at 163 °C [61]. No data on thermal studies of CPC were found in the literature. The experimental DTA curve of CPC monohydrate (see Fig. 2A) contains four endothermic effects, at 82, 177, 212, and 326 °C.

Defined amounts of as-synthesized CPPA (0.202 g) were placed in specialized quartz containers and heated to 400 °C. The DTA heating curve (see Fig. 2B) contains one endothermic effect, at 47 °C, and one exothermic effect, at 267 °C. The peaks in the heating curve of the CPPA do not match the thermal effects of the initial compounds. The exothermic effect corresponds to the decomposition of the CPPA sample, confirmed by the change in appearance (from yellow crystals to black powder and film) and weight loss ($\Delta m = 74.5\%$). The sharpness of the effect confirms the rapid decomposition of CPPA.

The second heating was performed to only 100 $^{\circ}$ C to prevent decomposition. Due to the absence of weight loss, the endothermic effect at 47 $^{\circ}$ C corresponds to the melting of CPPA.

The once-melted sample of CPPA was repeatedly investigated by DTA in a temperature range of 25–100 °C (see Fig. 2C). In the heating curves, one additional endothermic effect appears at 33 °C. Taking into account the absence of weight loss, the appearance of the additional endothermic peak can be explained by a polymorphic transformation. The endothermic peaks at 33 and 47 °C in the heating curve also agree with the exothermic effects in the cooling curve.

3.3. XRD analysis

The phase content of CPPA and CPC monohydrate was investigated by XRD. XRD powder patterns of as-synthesized CPPA, oncemelted CPPA, and CPC monohydrate are shown in Fig. 3. Analysis of the phase composition of CPC monohydrate was carried out by comparing the experimental diffraction pattern with data from the literature [62]. The CPC monohydrate diffraction pattern is characterized by the presence of only one system of reflexes which corresponds to triclinic crystal system or symmetry.



Fig. 3. Powder XRD diffraction patterns of as-synthesized CPPA (A), CPPA after heating (B) and CPC monohydrate (C).

Analysis of the phase composition of CPPA was carried out by comparing the experimental diffraction pattern with the simulated diffraction patterns of CPC monohydrate and picric acid [63]. The absence of the initial phase's peaks indicates the identity of the obtained compound. The powder pattern of CPPA reveals sharp diffraction peaks, and the crystallinity of the investigated sample is 75%. Indexing of obtained powder pattern indicates that the asgrown CPPA crystals are a monoclinic crystal system with the following cell parameters: a = 12.88 Å, b = 19.47 Å, c = 11.29 Å, $\beta = 103.58^{\circ}$, with cell volume V = 2753 Å³. Based on the obtained cell volume and density measurements (d = 1.2075 g/cm³), the number of formula units Z was determined to be 4.

Analysis of the melted CPPA sample powder pattern (Fig. 3B) indicates differences between its diffraction pattern and that of as-synthesized CPPA (Fig. 3A). Considering both heating curves (Fig. 2B and C), it can be noted that a high-temperature polymorphic modification of CPPA occurs during synthesis from solution; this indicated by the presence of only one endothermic effect in the heating curve. After melting, an additional peak appears (Fig. 2C), which corresponds to phase transformation. Thus, the CPPA recrystallizes in a low-temperature modification.

However, the diffraction peaks of high-temperature modification can be detected in low-temperature modification diffraction patterns due to the low melting point, slow crystallization rate, and high viscosity of the CPPA melt. Determination of the lattice parameters of the low-temperature modification CPPA sample was not possible due to the complexity of the separation of the reflex systems belonging to the high- and low-temperature modifications.



Fig. 4. FT-IR ATR spectra of solid-state CPPA, and CPPA in solutions of DMSO, chloroform.

3.4. FT-IR spectroscopy

FT-IR ATR spectra of CPPA were recorded for the solid-state sample and three solutions with solvents of different polarities: DMSO, chloroform, and *p*-xylene (Fig. 4). The signals of the pure solvents were subtracted from the recorded solutions' data. The characters of all spectra are similar, with only a marginal difference of some peaks' intensities, which testifies the same CPPA structure is present in different phases. m and *p*-xylene. The computed FT-IR spectrum of structure **C** is marked as DFT.

To assign the experimental peaks, we compared the experimental solid-state CPPA spectrum with the DFT-computed wavenumbers for structure **C** (Fig. 4). Weak peaks in the region 3069– 3126 cm⁻¹ (computed modes 225, 226, and 227 with corresponding frequencies of 3153, 3158, and 3159 cm⁻¹, respectively) were assigned to C–H stretching of PA and pyridinium ring. Two experimental medium bands at 2915 and 2849 cm⁻¹ correspond to asymmetric and symmetric C–CH₂ stretching vibration of the cetyl chain, respectively. The corresponding calculated modes 190–203 (symmetric) and 204–222 (asymmetric) are characterized by frequency ranges from 2937 to 2956 cm⁻¹ and from 2958 to 3057 cm⁻¹, respectively. Most intense symmetric and asymmetric cetyl chain C–H stretching vibrations in the calculated IR spectrum are represented by modes 203 and 217, with respective frequencies of 2956 and 3007 cm⁻¹.

A medium-broad peak at 1642 cm⁻¹ corresponds to the C–O stretching of PA. Computed mode 187 corresponds to this C–O vibration with frequency of 1625 cm⁻¹. Medium sharp signals at 1642 cm⁻¹, 1637 cm⁻¹, 1624 cm⁻¹, and 1610 cm⁻¹ are caused by the C–C stretching in both aromatic rings. The corresponding computed modes 188 (symmetric, pyridinium), 187 (symmetric, PA), 186 (asymmetric, pyridinium) and 185 (asymmetric, PA) have frequencies of 1631, 1625, 1573 and 1570 cm⁻¹, respectively. Visual analysis of mode 187 indicates that C–C stretching coincides with the intense C–O stretching.

A medium sharp peak at 1547 cm⁻¹ caused by asymmetric O– N–O bending. Related computed modes 231 and 232 are characterized by frequencies of 1552 cm⁻¹ and 1562 cm⁻¹, respectively. The rocking vibrations of the pyridinium ring are observed as a strong peak at 1483 cm⁻¹, whereas the scissoring C–C–H vibrations appear as a medium peak at 1471 cm⁻¹. A sharp medium peak at 1433 cm⁻¹ corresponds to C–C stretching in PA. Two bands, at 1364 cm⁻¹ and 1334 cm⁻¹, could be attributed to O–N–O symmetric stretching vibrations. Calculated modes 141 and 148, with frequencies of 1288 cm⁻¹ and 1316 cm⁻¹, respectively, correspond to these vibrations. The most intense experimental peak at 1274 cm⁻¹, according to the DFT-computed spectrum, can be assigned to the rocking vibration of the C–C(O)–C group, with the corresponding calculated mode 137 characterized by frequency of 1281 cm⁻¹.

The peaks at 1157, 1182, and 1073 cm⁻¹ are related to in-plane aromatic C–H deformation of the PA benzene ring. The C–NO₂ stretching vibrations are seen as two low-intensity peaks at 908 and 928 cm⁻¹. Two sharp medium peaks at 787 cm⁻¹ and 778 cm⁻¹ correspond to the out-of-plane vibrations of aromatic C–H groups.

The calculated IR spectra of structures **A**–**D** are presented in the supplementary material.

3.5. NMR study

NMR spectra of CPPA were recorded in $(CD_3)_2SO$ and compared with the NMR spectra of CPC. Figs. 5 and 6 show ¹H NMR and ¹³C NMR spectra of CPPA overlapped with the corresponding spectra of CPC.

The two protons of PA appear in the spectrum as a sharp singlet at 8.58 ppm (marked with a star in Fig. 5). The signal of the *o*-protons of the pyridinium ring appears at 9.08 ppm (doublet), which is upfield by about 0.20 ppm in comparison to CPC. At 8.60 ppm, the triplet of the *p*-proton is present, and only 0.03 ppm upfield relative to CPC. The chemical shift of the triplet of the pyridinium *m*-protons is 8.15 ppm, whereas in the CPC spectrum, the corresponding signal is located at 8.18 ppm.

Chemical shifts of cetyl chain protons in CPPA and CPC molecules are well-matched, except the signal of the α -methylene group. In the case of CPPA, the α -CH₂ group signal shows as a triplet at 4.58 ppm, whereas, in the case of CPC, the signal of the same group appears at 4.68 ppm. The chemical shift of the β -CH₂ group protons shifts upfield and appears as a multiplet at 1.90 ppm. The signal of the preterminal methylene group is present at 1.26 ppm, overlapping with the intense signal at 1.22 ppm that corresponds to protons attached to C₃-C₁₄ carbons of the cetyl chain. The peak of the terminal methyl group of the cetyl chain appears as a triplet at 0.84 ppm.

The signal at 160.80 ppm corresponds to the C–O carbon of PA (see Fig. 6). Peaks at 141.83, 125.15, and 124.10 ppm correspond to the *o*-, *m*- and *p*-carbons of PA, respectively. Signals of *p*-, *m*- and *o*-carbons of pyridinium ring appear at 145.43, 128.06, and 144.71 ppm, respectively. A peak of the α -methylene group appears at 60.78 ppm. Signals of the cetyl chain C₂–C₁₆ carbons are present in the upfield region. Two close peaks at 31.28 and 30.71 ppm correspond to the C₂ (β -methylene group) and C₁₄ carbons, respectively. The six peaks in the range 28.36–29.03 ppm correspond to the C₄–C₁₃ carbons. A signal of the γ -methylene group appears at 25.39 ppm. In the most upfield region, the signals of preterminal and terminal carbons of the cetyl chain appear at 22.07 and 13.89 ppm, respectively.

We must spotlight the perfect match of chemical shifts of CPPA and CPC, except in the cases of pyridinium o-carbons and α methylene group. In contrast to CPC, the CPPA signals of the ocarbons and α -CH₂ group are shifted upfield by 0.14 and 0.28 ppm, respectively. The differences are marginal but rather high in comparison to other signals; similar upfield shifts of CP NMR peaks were observed in our previous work [15].

These upfield shifts can be caused by electron shielding of the pyridinium ring via charge transfer (CT) interaction with the electron-donating PA. Numerous works have indicated the



Fig. 5. Overlapped ¹H NMR spectra of CPPA and CPC.



Fig. 6. Overlapped ¹³C NMR spectra of CPPA and CPC.

Table 2

The number of donated electrons from PA to CP – d(PA); electrons back donated from CP to PA – b(CP); net electron transfer values calculated via ECDA. Net charge difference (NCD) calculated with Hirshfeld partial charges.

	d(PA)	b(CP)	d(PA)-b(CP)	ECDA	NCD
A	0.1066	-0.0095	0.1161	0.1469	0.204
C	0.1642	-0.0012	0.1660	0.1995	0.299
D	0.1026	-0.0084	0.1110	0.1388	0.195

presence of CT interactions in organic picrates [64,65]. A complex DFT study was performed to explore CT interactions in CPPA. The superior performance of range-separated density functionals versus single hybrid functionals in the description of CT processes and interactions is well-known. That is why we have used the range-separated wB97X functional in combination with the 6–311G(d,p) basis set for the generation of electron densities of structures **A–D** and the corresponding separate ions.

Analysis of the electron density differences between the CPPAassociated and separate CP and PA ions indicate the electron density transfer from PA to the *o*-hydrogens of the pyridinium ring and α -methylene group (see supplementary materials). For quantitative analysis of CT, charge decomposition analysis (CDA) [66] and its extended form (ECDA) [67] were performed in Multiwfn (see Table 2). The extent of electron donation (denoted as d(PA)) from PA to CP via the corresponding complex orbital is in the range of 0.1026–0.1642.

In contrast, the number of electrons back-donated (denoted b(CP)) from CP to the anion has negligible values, from -0.0112 to -0.0018, and the negative values indicate the higher acceptor.

tor, rather than donating, properties of CP. The difference between d(PA) and b(CP) can be considered as the number of net electrons transferred from PA to CP due to the formation of the corresponding complex orbital. The ECDA method was employed to calculate net electron transfer values without the contribution of the electron polarization effect. These values (from 0.1388 to 0.1995) indicate the transferring of electron density from PA to CP, and explain the experimentally observed electron shielding of the α -methylene group and *o*-hydrogens of the CP ion.

Moreover, the quantity of electrons transferred between two fragments was calculated by the net charge difference (NCD) approach. The partial charge of fragments (CP and PA) were calculated by summing all atomic charges in the ion and then subtracted from the charge of an isolated ion. The Hirshfeld charges were used for the investigation of CT effects via NCD calculation. The net charge difference values in Table 2 represent the number of electrons donated from the PA to CP. The observed values in the range 0.195–0.299 testify to the significant CT effect. We found a good correlation between all approaches (CDA, ECDA, and NCD) used for the quantitative analysis of CT effects.

The NMR spectra described above give a general picture of the CPPA structure and interactions between the ions. However, to exclude possible solvent effects on the CPPA structure, the samples of the ionic liquid were explored using solid-state ¹H and ¹³C cross-polarization/MAS/DD NMR techniques. Overlapped ¹H MAS NMR spectra of CPC and CPPA are presented in Fig. 7. In the case of CPC, the spectrum contains a very broad area with only two identifiable small peaks at 1.35 ppm and 3.55 ppm. These correspond to the hydrogen atoms of the cetyl chain and the hydrogen atoms of the co-crystallized water molecule, as the monohydrated form of CPC was used in this study. The broad area at about 7 ppm relates to the pyridinium hydrogen atoms. In the case of CPPA, the spectrum



Fig. 7. Overlapped (unnormalized) solid-state ${}^{1}\mathrm{H}$ MAS NMR spectra of CPPA and CPC.

contains relatively sharp peaks at 1.16 ppm, 5.08 ppm, 8.62 ppm, and 11.56 ppm, which correspond to the cetyl chain protons, the two protons of the N–CH₂ group, pyridinium and the PA rings hydrogen atoms, respectively. In MAS NMR studies, broader peaks indicate lower internal mobility of atomic groups in the molecule, whereas sharp signals indicate higher mobility. Consequently, the CPC spectra indicate a relatively fixed internal structure, while the spectra of CPPA ionic liquid with flexible and rotatable structure contains relatively sharp peaks.

Similarly, in the case of ¹³C cross-polarization/MAS/DD NMR (Fig. 8), the relatively narrow signal at 16.46 ppm indicates the high mobility of the corresponding methyl group. The broad area from 24.40 to 34.41 ppm is caused by the overlapping of signals of similar carbons of the cetyl chain. The broadness of the N–CH₂ group of peaks at 61.87–63.17 ppm is caused by cetyl chain disorder due to its flexibility, as shown in the discussion of DFT calculations above. Peaks in the range of 124.80–148.94 ppm correspond to the carbons of the pyridinium and PA rings. The most downfield signal, at 164.13 ppm, is related to the C–O group of the PA carbon atoms.

3.6. Conductometric study

Many compounds with long or bulky ions, such as ILs or surfactants, can aggregate and form micelles [68]. In order to investigate the possible influence of ion association and micelle formation on the NMR chemical shifts, conductometric studies were performed. Electrical conductivity measurements can be used for the direct determination of critical micelle concentrations (CMC) [69]. Most of the conductometric studies related to CPC micelle formation (CMC, energetic parameters) are deal with dilute (10⁻³–10⁻⁴ mol/L) water–polar organic binary mixtures [70,71].

Table 3

Molar conductivities at infinite dilution (Λ_{∞}) and association constants (K_A) for solutions of CPPA and CPC in DMSO at different temperatures.

	Λ_{∞} , S×c	cm ² /mol	K _A , L/mol		
lemperature, °C	CPPA	CPC	CPPA	CPC	
22	38.3	37.3	748.7	525.0	
30	36.6	35.6	695.0	436.2	
40	34.3	35.1	508.3	439.8	
50	33.6	33.7	467.1	351.3	

The specific conductance of CPC and CPPA (see supplementary materials) solutions in the concentration range 2.510^{-4} – 1.610^{-1} mol/L increases linearly with increasing solute content. The specific conductance of the investigated solutions decreases with increasing temperature. In all cases, the conductance of CPC solutions is slightly higher than that of the corresponding CPPA solutions, and this phenomenon can be related to the higher molar ionic conductivity of the chloride anion in comparison to the PA [72].

The slopes of the plots of the concentration dependence of specific conductivity against the total concentration of CPC and CPPA do not contain sharp differences. The molar conductivity (Λ_m) for CPC and CPPA in DMSO was calculated to determine the CMC (molar conductivity can be calculated as $\Lambda_m = \kappa / C_M$). Fig. 9 presents the values of molar conductivity obtained at different temperatures as a function of the molar concentration square root ($C_M^{1/2}$) of CPC and CPPA. The molar conductivity in both cases decreases with the concentration increase.

The DMSO solutions of CPC are characterized by two values of CMC: The first occurs in a dilute region and refers to micelle formation. The value of CMC (0.01 mol/L) does not depend on temperature. The second CMC is related to a change of micelle type, and it is sensitive to temperature change. Thus, at 22 and 30 °C, the CMC is 0.14 mol/L, whereas at 40 and 50 °C, it is 0.12 mol/L.

The above relationships were used to calculate the limiting molar conductivity (Λ_{∞}) and related standard-state association constants (K_A). Ostwald's dilution law combined with the Arrhenius relation [73] enables the determination of the limiting value of the molar conductivity (Λ_{∞}) (Eq. (1)).

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_\infty} + \frac{K_A}{\Lambda_\infty^2} \times \Lambda_m \times C_M \tag{1}$$

For these purposes, the linear form of the Ostwald's dilution law was plotted in the form of $1/\Lambda_m = f (c \times \Lambda_m)$. Extrapolation of the line to the zero concentration point gives the required value of Λ_∞ .

The ion-pair formation is characterized by the association constant K_A . Table 3 summarizes derived molar conductivities at infi-



Fig. 8. ¹³C solid-state cross-polarization/MAS/DD NMR spectra of CPPA.



Fig. 9. Molar conductivity dependence of CPC (A) and CPPA (B) concentration in DMSO.

nite dilution (Λ_{∞}) and related standard-state association constants (K_A) . The K_A values are relatively large, in comparison to similar ionic liquids [74], which testifies the higher association in the case of CP salts. Moreover, at all tested temperatures, ions in CPPA seems to be more associated than in CPC.

In the case of CPPA DMSO solution, the first CMC value remains constant (0.02 mol/L) at all examined temperatures. The second CMC of CPPA solutions equals 0.08 mol/L and 0.1 mol/L at 22 °C and 30 °C, respectively. The similar behavior of micelle formation of CPC and CPPA solutions is probably determined by the surfactant properties of the CP cation.

4. Conclusions

The ion pair of cetylpyridinium cation with picrate anion is an above room temperature ionic liquid was synthesized and the structure was determined using XRD, FT-IR, and NMR methods. DTA results established that the investigated compound congruently melts at 47 °C, and remains a liquid up to 267 °C. Vigorous decomposition was observed at higher temperatures. CPPA undergoes a polymorphic transformation at 33 °C. The two different modifications were obtained when CPPA was crystallized from a solution or during recrystallization from a melt.

The differences of about 0.2 ppm and 0.1 ppm in H–NMR chemical shifts' of the *o*-protons and the α -methylene group protons of CPPA and CPC can be explained by: (a) high interionic chargetransfer effects caused by the electron-donating picrate anion in the case of CPPA, which were established via the DFT-based investigation of CDA, ECDA, and the net charge differences; (b) higher ion association in the case of CPPA DMSO solution in comparison to CPC, which can be concluded from the K_A values of 748.7 L/mol and 525.0 L/mol, respectively.

Additionally, during the conductivity study, two values of CMC were determined for CPPA and CPC DMSO solutions. Given the determined CMC values of CPC and CPPA are lower than the concentrations of the solutions studied by NMR, it can be assumed that the experimentally observed peak differences in NMR spectra are due to the donating (shielding) activity of the PA anion rather than micelle formation.

Analysis of resonance structures of picrate anion shows negative charge delocalization over all oxygen atoms and explains picrate's ability to establish different coordination modes with the cation. The presence of a double bond between the phenolic oxygen and the carbon atoms of the picrate ring was confirmed through Mayer bond-order analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Maksym Fizer: Conceptualization, Supervision, Investigation, Writing - original draft, Writing - review & editing. **Michael Filep:** Conceptualization, Investigation, Writing - original draft, Writing - review & editing. **Oksana Fizer:** Conceptualization, Investigation, Writing - original draft. **Orga Fričová:** Investigation, Writing original draft. **Ruslan Mariychuk:** Conceptualization, Investigation, Writing - original draft, Writing - review & editing.

Acknowledgments

This study was partially supported by the Ministry of Education and Science of Ukraine [Projects GR-0119U100232 and GR-0120U100431], and by the Slovak Academic Information Agency (National Scholarship Programme of the Slovak Republic, Grants ID 25718 and 30750].

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129803.

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