

Novel triazine-functionalized tetra-imidazolium hexafluorophosphate salt: Synthesis, crystal structure and DFT study

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Highlights

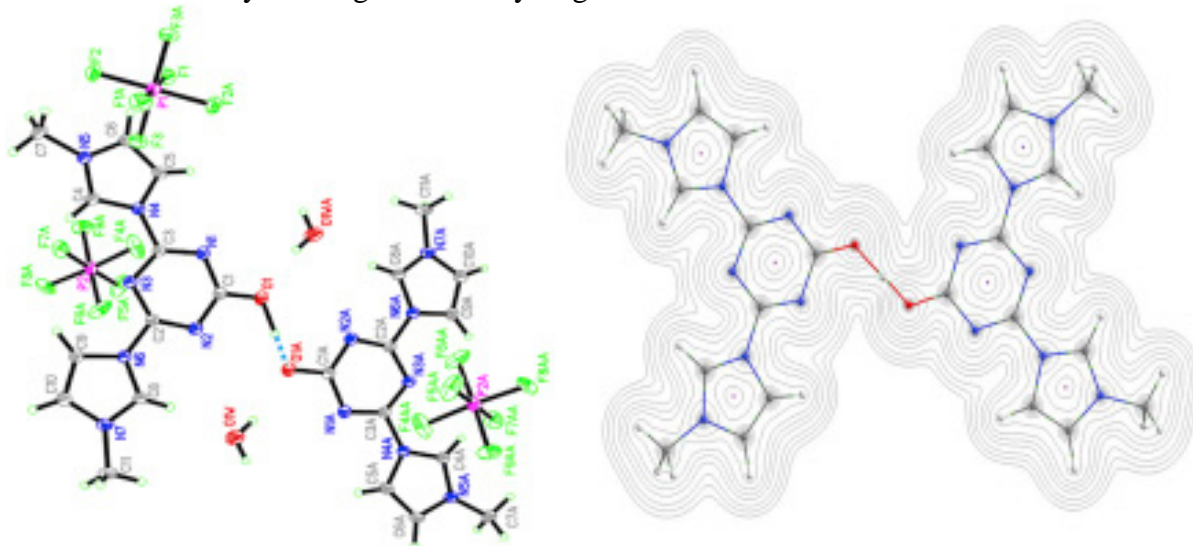
- Novel triazine-functionalized tetra-imidazolium hexafluorophosphate salt.
- The structure was confirmed by X-ray technique.
- X-ray diffraction revealed a unique structure.
- DFT was used to have molecular insight into the structure.

Abstract

A novel triazine-functionalized tetra-imidazolium hexafluorophosphate salt was synthesized by the reaction of N-methylimidazole with cyanuric chloride under a nitrogen atmosphere. The prepared compound was characterized by ¹H & ¹³C NMR, CHN analysis, and single crystal X-ray technique. X-ray diffraction data revealed an essentially planar structure with two identical moieties of the title compound linked by a strong O–H···O hydrogen bond. Density functional theory method was used to have molecular insights into the structure and bonding of the compound.

Graphical abstract

Novel triazine-functionalized tetra-imidazolium hexafluorophosphate salt was synthesized and characterized. X-ray diffraction data revealed a unique structure as two identical moieties of the salt linked by a strong O–H···O hydrogen bond.



Keywords: Triazine; Cyanuric chloride; Imidazolium salts; X-ray; NMR spectroscopy; DFT

1. Introduction

Imidazole is an aromatic 5-membered ring containing two nitrogen atoms in the 1- and 3-positions. Imidazole analogue systems are present as a part in several important natural products, such as histidine, histamine, purine and nucleic acids. Due to the high therapeutic properties, imidazole derivatives have occupied a unique place in the field of medicinal chemistry and have been used as a building block to synthesize a large number of novel chemotherapeutic agents [1]. Furthermore, imidazole derivatives show various pharmacological activities including anti-fungal, anti-bacterial, anti-cancer, anti-tumor, anti-viral, anti-inflammatory and analgesic activity [[2], [3], [4], [5]]. Upon substitution of both nitrogen atoms of the imidazole ring, imidazolium salts are obtained. These salts have been used as ligand precursors for N-heterocyclic carbenes, which are popular ligands for transition metal complexes employed in catalysis.

Cyanuric chloride or cyanuryl chloride (2,4,6-trichloro-1,3,5-triazine) is a white, easy hydrolytic degradation powder of pungent odor. It is soluble in different organic solvents, but nearly insoluble in water. Cyanuric chloride possesses three reactive positions that can be selectively substituted by nucleophiles, such as primary and secondary amines [6]. It is worth noting that cyanuric chloride tends to hydrolyze in water to produce 2,4-dichloro-6-hydroxy or 2-chloro-4,6-di-hydroxy or 2,4,6-trihydroxy derivatives [[6], [7], [8]]. Cyanuric chloride is typically used as an organic intermediate to produce triazine derivatives which have been widely used in the dye industry, agriculture chemistry, plastic, and rubber industry [9].

Due to their promising biological activity, triazines and their derivatives represent an important class of compounds. They are known to be anti-protozoals, anti-cancer agents, anti-

malarials, and anti-microbials [10]. Herein, we present the synthesis, characterization and crystal structure of novel triazine-functionalized tetra-imidazolium hexafluorophosphate salt. It was synthesized by the reaction of cyanuric chloride with N-methylimidazole followed by metathesis reaction with KPF₆. Notably, an X-ray diffraction study revealed a unique structure as two identical moieties of the prepared compound linked by hydrogen bond containing positively polarized hydrogen between negatively polarized oxygens. Density functional theory (DFT) methods were also used to supplement the experimental work.

2. Experimental

2.1. Materials and measurements

All chemicals and solvents were obtained from commercial sources and used without further purification. N-methylimidazole, cyanuric chloride and potassium hexafluorophosphate were purchased from Sigma-Aldrich. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz Ultrashield™ spectrometer at ambient temperature using CD₃CN solutions. Chemical shifts were referenced to the internal residual solvent impurity at δ_H 1.94; or carbon signals at δ_C 1.32 (CH₃CN) or 118.26 (CH₃CN). Elemental analysis was carried out on a PerkinElmer Series II, 2400 microanalyzer. X-ray diffraction data were collected using a Bruker SMART APEX2 CCD area-detector diffractometer. All the above mentioned instruments are available at the School of chemical sciences and School of Physics, University Sains Malaysia (USM).

2.2. Synthesis of the tetra-imidazolium salt (4)

In a 150 ml round bottom flask connected to N₂ and charged with magnetic stirrer, 1-methylimidazole (0.3 g, 3.6 mmol) in 20 ml of dried acetone was added. The flask was immersed in an ice bath, and cyanuric chloride (0.2 g, 1.08 mmol) in 20 ml of dried acetone was added dropwise. An off-white precipitate was formed immediately. The stirring was continued for 1 h in an ice bath and 4 h at ambient temperature. The precipitate was collected by filtration and washed with fresh acetone (2 × 5 ml) and then KPF₆ (0.7 g, 3.8 mmol) in 25 ml of distilled water was added, the mixture was stirred for 1 h and left standing overnight. The precipitated white solid was filtered and washed with distilled water (3 × 5 ml) and left to dry at ambient temperature. The yield was (0.62 g, 57.83%), m.p = 270–272 °C. Crystal suitable for X-ray analysis was obtained by slow evaporation of the salt solution in acetonitrile at ambient temperature. ¹H NMR (400 MHz, CD₃CN): δ 3.41 (1H, s, O–H), δ 4.01 (6H, s, CH₃–N), 7.59 (2H, t, ³J_{HH} = 6 Hz, imidazolium H5'), 8.26 (2H, t, ³J_{HH} = 6 Hz, imidazolium H4'), 9.57 (2H, s, imidazolium H2'); ¹³C {1H} NMR (100 MHz, CD₃CN): δ 37.32 (CH₃), 119.54, 120.14 (imidazolium C5' & C4'), 123.60 (imidazolium C2'), 126.0 (2 × triazine NCN), 137.32 (triazine C–O). Anal. Cal. For C₂₂H₂₅F₁₈N₁₄O₂P₃ · H₂O: Cal.: C, 27.23; H, 2.80; N, 20.21%. Found: C, 27.38; H, 3.02; N, 20.13%.

2.3. X-ray crystallography

Single crystal diffraction measurements were made using Bruker APEX2 DUO CCD area-detector diffractometer. The data were collected at 293 K with a MoKα micro focus source (λ = 0.71073 Å). Data reduction was performed using SAINT+ [11] and the intensities were corrected for absorption using SADABS [10]. The structure was solved by direct methods using SHELXT [12] using the SHELXL-2014/7 program, and refined by full matrix least-squares techniques on F₂ with SHELXL [13]. All hydrogen atoms (except those involved in

hydrogen bonds) were positioned geometrically and were refined using a riding model. The data quality was good enough to locate the hydrogen-bonded hydrogen atoms (alcohol and water moieties) on the Fourier difference synthesis and to refine them reasonably.

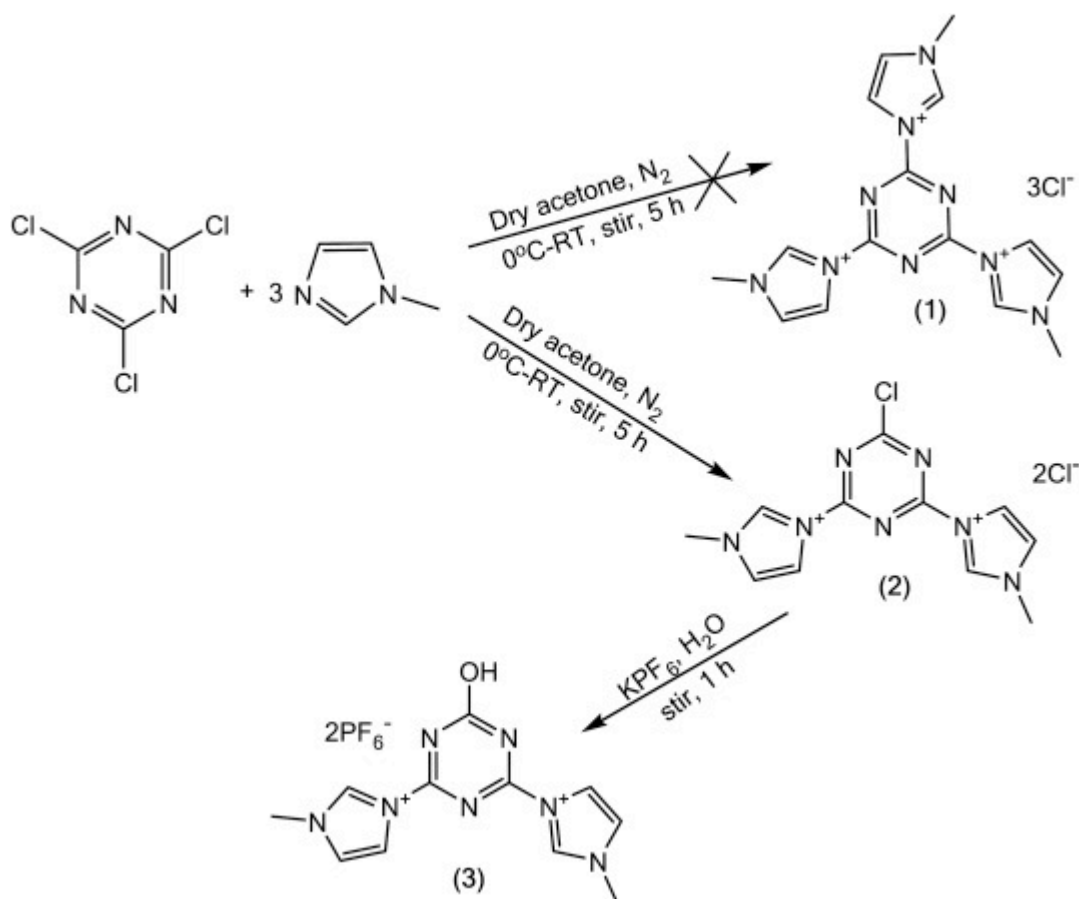
2.4. Computational details

All calculations were carried out using DFT with the B3LYP hybrid functional [14,15] in the gas phase using the Gaussian 09 program [16]. The triple- ζ basis set 6-311G(d,p) basis set was used for all atoms (C, H, N, O) [17]. The gas phase (298.15 K and 1 atm) and solvent interaction (CH₃CN) geometries of all intermediates were fully optimized at the same level of theory without any symmetry restrictions, ensuring that the local minima had zero imaginary vibrational frequencies [18] and to provide the thermal correction to free energies. AIMAll version 17.11.14 [19] was used to calculate topological properties, QTAIM molecular graphs, as well as atomic populations. QTAIM analyses were performed using the Gaussian checkpoint files from the abovementioned optimized calculations.

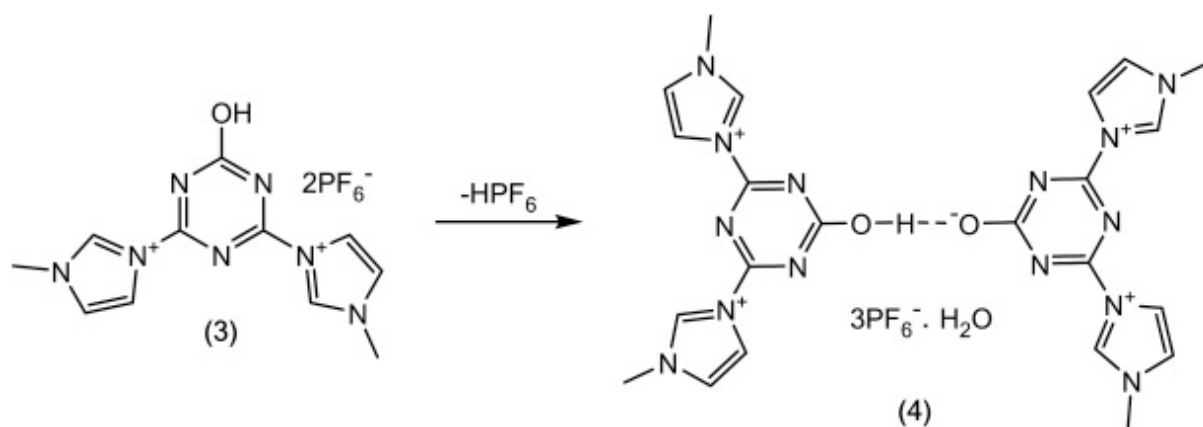
3. Results and discussion

3.1. Synthesis of compound 4

Compound 4 was prepared according to the procedure reported in our previous work with slight modification [[20], [21], [22]]. Reactions involved in the preparation of the compound presented in this work are shown in Scheme 1, Scheme 2. The reaction of cyanuric chloride with three equivalent of N-methylimidazole in dry acetone under nitrogen atmosphere for 5 h was conducted to prepare 2,4,6-tris(1-methylimidazolium-3-yl)-1,3,5-triazine chloride 1. However, instead of 1, 2-chloro-4,6-bis(1-methylimidazolium-3-yl)-1,3,5-triazine chloride 2 was produced as solid off-white precipitate, which was filtered and washed with fresh dry acetone. The resulted salt was converted to its corresponding hexafluorophosphate counterpart *via* a salt metathesis reaction with KPF₆ in distilled water. As a result, compound 2 was hydrolyzed to give 2-hydroxy-4,6-bis(1-methylimidazolium-3-yl)-1,3,5-triazine hexafluorophosphate 3. Finally, two molecules of 3 spontaneously condensed to give the tetraimidazolium dimer 4 as a white solid which was collected and washed with distilled water and left to dry at ambient temperature.



Scheme 1. Synthesis of compound **3**.



Scheme 2. Condensation of **3** to produce **4**.

3.2. NMR data of compound **4**

The ^1H NMR spectrum of compound **4** was recorded in $d_3\text{-CD}_3\text{CN}$ over the range δ_{H} 0–11 (Figure S11 in the Supplementary Information). The acidic imidazolium protons (H2') appeared as a singlet sharp peak at δ_{H} 9.57. The imidazolium backbone protons (H5' and H4') appeared as two triplets at δ_{H} 7.59 and 8.26 ppm (each with $^3J_{\text{HH}} = 6$ Hz), respectively. A broad singlet corresponding to the hydrogen-bonded in **4** appeared at δ_{H} 3.41. In the ^{13}C NMR spectra, the imidazolium C2' signal appeared at δ_{C} 123.6, while C5' & C4' appeared at δ_{C} 119.54 and δ_{C} 120.14, respectively. The triazine NCN carbon signal appeared at δ_{C} 126.0,

whereas the signal for C–O appeared as a singlet at δ_C 137.32 due to the highly symmetrical nature of the alcohol-alkoxy hydrogen-bonded dimer. This illustrates further how the strong hydrogen bond persists in solution, as well as in the solid state (see below).

3.3. Crystal structure of compound 4

The molecular structure of the compound **4** was confirmed by means of single crystal X-ray diffraction. Crystals suitable for the X-ray diffraction studies were obtained by slow evaporation of the salt solution in acetonitrile at ambient temperature. During the formation of compound **4**, the chloride in the disubstituted cyanuric chloride has undergone hydrolysis to form a hydroxyl unit [[6], [7], [8], [9],20]. Then, two of the hydrolyzed units are condensed to produce **4** as two identical moieties linked by hydrogen bridge, Scheme 1, Scheme 2. The above mentioned compound is crystallized in a monoclinic space group $P2_1/c$ with three hexafluorophosphate counterions and two water molecules. The organic molecule consists of two identical moieties containing the N-methylimidazolium functionalized disubstituted triazine. These two triazine moieties are linked by a strong [23] O–H \cdots O (H1–O1 = 1.22) hydrogen bond (Fig. 1). This hydrogen bond links two negatively polarized oxygens which can be formulated either as (O–H–O) or (O–H \cdots O $^-$). Collectively, the molecule is charge balanced with four charged methylimidazolium fragments (4+), three hexafluorophosphate anions (3-), as well as the alkoxy moiety (1-) linking the two triazine fragments. The linked moieties and water molecules are all essentially co-planar with C3–N1–C1–O1 = 179.90(8) $^\circ$ and N1–C1–O1–H1 = 178.34 $^\circ$. Interestingly, the hexafluorophosphate anions are all out of plane, despite noticeable bifurcate O–H \cdots F (H1WA–F3 = 2.18 Å) and C–H \cdots F (H5–F3 = 2.32 Å) interactions. In the crystal structure, the slightly shorter bond length of O1–H1 (1.22 Å) as compared to O1–C1 (1.2858(17) Å) are expected for an organic alcohol group, and correlate well with related compounds [24]. Within each triazine heterocycle, a slightly distorted 6-membered ring is observed with varying C–N bond distances ranging between 1.3105(18)-1.3544(19) Å. Amongst the latter C–N bond lengths, the bond distances of N1–C1 (1.3540(19) Å) and N2–C1 (1.3544(19) Å) are the longest within the range, which are adjacent to the O–H \cdots O $^-$ moiety. The bond angle of C1–O1–H1 is 116.00 $^\circ$, while the O1–C1–N1 and O1–C1–N2 bond angles are 117.11(12) $^\circ$ and 119.21(13) $^\circ$, respectively. The distortion within the triazine ring is further highlighted through the bond angles of N1–C1–N2 (123.68(13) $^\circ$), N2–C2–N3 (129.34(13) $^\circ$), and N3–C3–N1 (129.42(13) $^\circ$) exhibiting slightly larger than expected N–C–N bond angles. In contrast, slightly smaller than typical C–N–C bond angles of C1–N2–C2 (113.60(12) $^\circ$), C2–N3–C3 (110.39(12) $^\circ$), and C3–N1–C1 (113.53(12) $^\circ$) were observed. Furthermore, the hexafluorophosphate anions link the cations into a three-dimensional network *via* an intermolecular C–H \cdots F hydrogen bond interactions, as shown in unit cell packing of the compound **4** (Fig. 2) [[25], [26], [27]]. The resultant organic moieties are then arranged in layers within the crystal structure, with a centroid-centroid distance of *ca.* 5.969 Å (\sim 21.05 $^\circ$ consecutive incline) along the c-axis. Crystal data, structure refinement details, selected bond distances and angles of compound **4** are tabulated in Table 1, Table 2, respectively.

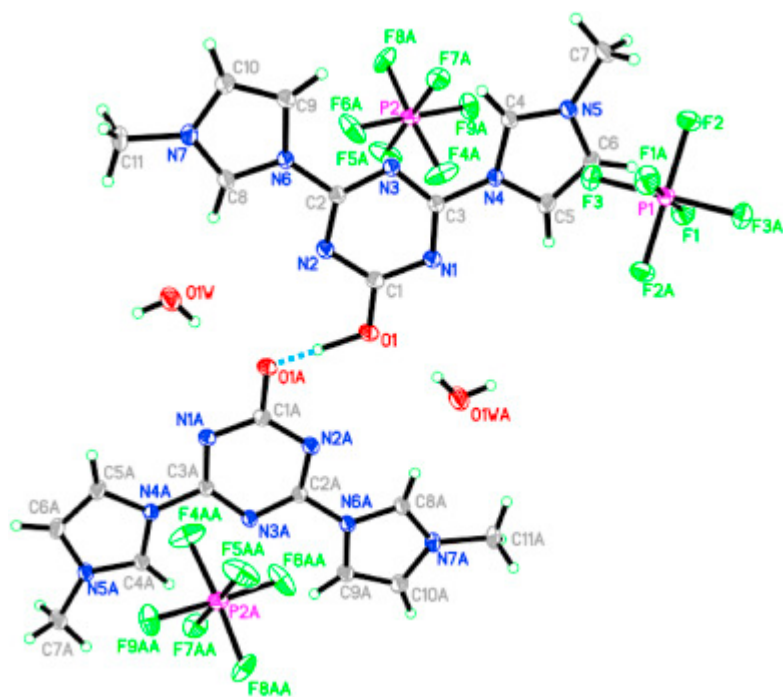


Fig. 1. Crystal structure of **4** with displacement ellipsoids drawn at 50% probability. The hydrogen bond linking the two triazine moieties are indicated by the cyan dotted line.

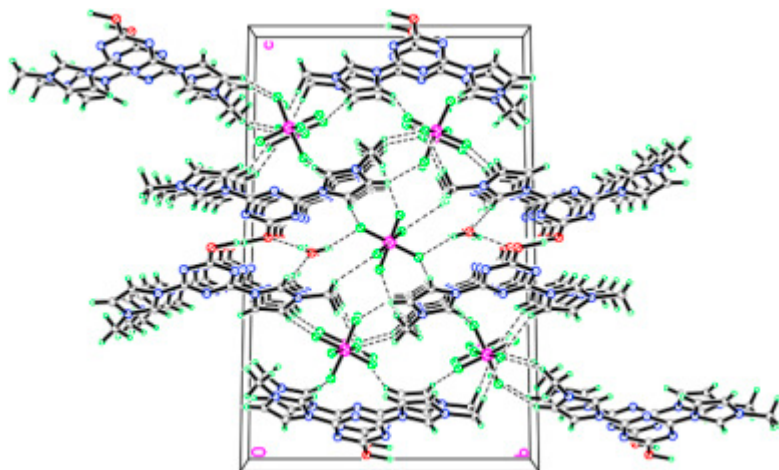


Fig. 2. Crystal unit cell packing of **4**.

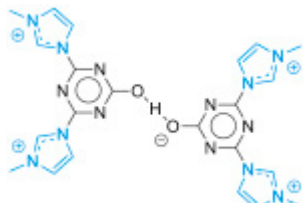
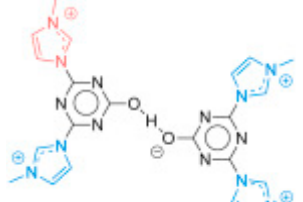
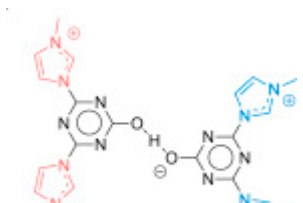
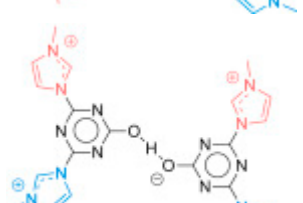
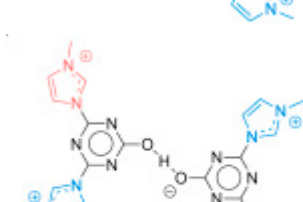
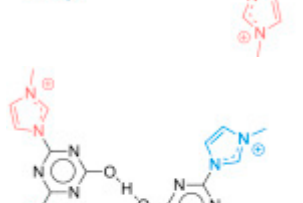
Table 1. Crystal data and structure refinement of **4**.

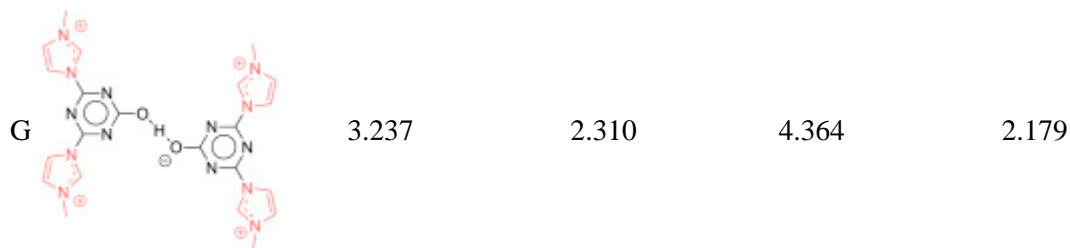
C ₂₂ H ₂₅ N ₁₄ O ₂ , 3(PF ₆), 2(H ₂ O)	Formula
988.50	Formula Weight
Monoclinic	Crystal System
P21/c (No. 14)	Space group
5.9689(5), 14.1527(13), 22.5928(19)	a, b, c [Å]
90, 105.176(3), 90	α, β, γ [°]
1842.0(3)	V [Å ³]
2	Z
1.782	D _{calc} g/cm ³
0.308	Mu(MoKa) [/mm]
996	F(000)
0.08 × 0.11 × 0.44	Crystal Size [mm]
293	T (K)
MoKa 0.71073	Radiation [Å]
1.7, 32.5	Theta Min-Max [°]
−8: 9; −20: 21; −34: 34	Dataset
28035, 3127, 0.0372	Tot., Uniq. Data, R(int)
3127, 334	Nref, Npar
0.0248, 0.0659, 1.0440	R, wR2, S

Table 2. Selected bond lengths (Å) and angles (°) of **4**.

Bond lengths (Å)			
1.3544(19)	N2–C1	1.2858(17)	O1–C1
1.3206(18)	N3–C2	1.2200	O1–H1
1.3315(18)	N3–C3	1.3105(18)	N1–C3
1.4158(18)	N4–C3	1.3540(19)	N1–C1
1.4191(18)	N6–C2	1.3167(18)	N2–C2
Bond angles (°)			
115.70(12)	N2–C2–N6	116.00	C1–O1–H1
114.96(11)	N3–C2–N6	113.60(12)	C2–N2–C1
129.42(13)	N1–C3–N3	117.11(12)	O1–C1–N1
115.97(12)	N1–C3–N4	123.68(13)	N1–C1–N2
114.60(11)	N3–C3–N4	113.53(12)	C3–N1–C1
107.99(14)	N5–C4–N4	110.39(12)	C2–N3–C3
107.72(14)	N7–C8–N6	119.21(13)	O1–C1–N2
125.68(13)	C3–N4–C5	129.34(13)	N2–C2–N3

Table 3. Relative Gibbs free energies ($\text{kJ}\cdot\text{mol}^{-1}$) and energy gaps ($\text{kJ}\cdot\text{mol}^{-1}$) for the different conformations of **4**.

Conformer	Gas phase		Solvent correction (CH_3CN)	
	Relative Gibbs free energy ($\text{kJ}\cdot\text{mol}^{-1}$)	Relative energy gap ($\text{kJ}\cdot\text{mol}^{-1}$) ^b	Relative Gibbs free energy ($\text{kJ}\cdot\text{mol}^{-1}$)	Relative energy gap ($\text{kJ}\cdot\text{mol}^{-1}$) ^b
A 	3.214	16.068	2.770	8.428
B 	3.978	12.025	0.000	2.652
C 	0.428	2.074	1.405	0.788
D 	0.000	0.000	0.6301	3.308
E 	2.531	12.366	1.686	3.439
F 	0.824	4.805	3.253	0.000



3.4. DFT study of compound 4

The substitution of two molecules of N-methylimidazole to cyanuric chloride, and the subsequent condensation reaction to yield compound **4**, gives rise to seven unique conformations that compound **4** theoretically may assume in the solid state. These conformations are based on the direction of the acidic C(2)-imidazolium proton of each of the four imidazolium moieties face: either towards or away from the central hydrogen-bonded alkoxy-hydroxyl functionalities (Table 3). It was therefore of interest to determine whether other conformations of **4** is energetically favorable to exist in the solid state, and which isomer is associated with the global minimum energy. Table 3 contains the DFT-calculated relative Gibbs free energy ($\text{kJ}\cdot\text{mol}^{-1}$), and relative energy gaps ($\text{kJ}\cdot\text{mol}^{-1}$) of each of the cation conformers. In general, the energies and energy gaps of all calculated and optimized conformers were observed to fall within a narrow range of $4.3\text{kJ}\cdot\text{mol}^{-1}$ (Gibbs free energy) and $16.1\text{kJ}\cdot\text{mol}^{-1}$ (energy gap) when optimized in either gas phase or with solvent interaction (CH_3CN). This necessarily suggests that all considered conformers are possible to exist in the solid state. Since single crystals of **4** were grown from an acetonitrile solution, it is interesting to note that the predicted global energy minimum conformer **B** (CH_3CN interaction) does not correspond to the $E_{\text{rel}} = +2.8\text{kJ}\cdot\text{mol}^{-1}$ conformer **A** (conformer observed in the solid state). In addition, the energy gap ($E_{\text{HOMO}} - E_{\text{LUMO}}$) is often also considered when evaluating stable isomers or conformers [28]. In general, an isomer/conformer exhibiting the larger energy gap would correspond to the more stable or less reactive isomer/conformer. Evaluation of the relative energy gap revealed isomer **A** to be the least reactive and therefore most stable conformer for both in the presence and absence of CH_3CN solvent interactions, which indeed corresponds to the experimentally observed conformer.

From the molecular structure obtained from SCXRD (Fig. 1), the bridging hydrogen atom is observed at an equidistance away from both O1 and O1A because of it occupying a special position (rotation axis). A DFT-optimized structure of **4** (Fig. 3) shows a more accurate description of the $\text{O}-\text{H}\cdots\text{O}^-$ moiety with bond distances 1.122Å ($\text{O}-\text{H}$) and 1.311Å ($\text{H}\cdots\text{O}^-$). The optimized bond length and bond angle of **4** in the gas phase are provided in Table SII as part of the supplementary information. The dipole moment of Compound **4** was computed as 2.034 Debye. It has been reported that results that stem from NBO (Natural Bond Orbital) and QTAIM (Quantum Theory of Atoms in Molecules) calculations could collectively provide additional insight to the electron density within a hydrogen bond [29]. A significant NBO interaction within the $\text{O}-\text{H}\cdots\text{O}^-$ group is observed (Fig. 3(a)), showing how the complete $\text{O}-\text{H}\cdots\text{O}^-$ functional group is involved. This interaction was associated with an internal NBO stabilization energy of $18.24\text{kJ}\cdot\text{mol}^{-1}$. Furthermore, the QTAIM analysis of **4** revealed several BCP (Bond Critical Points) as well as RCP (Ring Critical Points) (Fig. 3(b)). BCPs typically indicate the region of space for which the shared electron density between two atoms in a bond is at a minimum along with the bonding direction, whereas RCP is an

extension of a BCP within a cyclic system where a saddle point of minimum electron density within the ring system exists. Interestingly, no other intramolecular stabilizing interactions between nitrogen and hydrogen atoms have been observed. All BCPs, RCPs, and electron densities are observed at expected positions and within expected amounts.

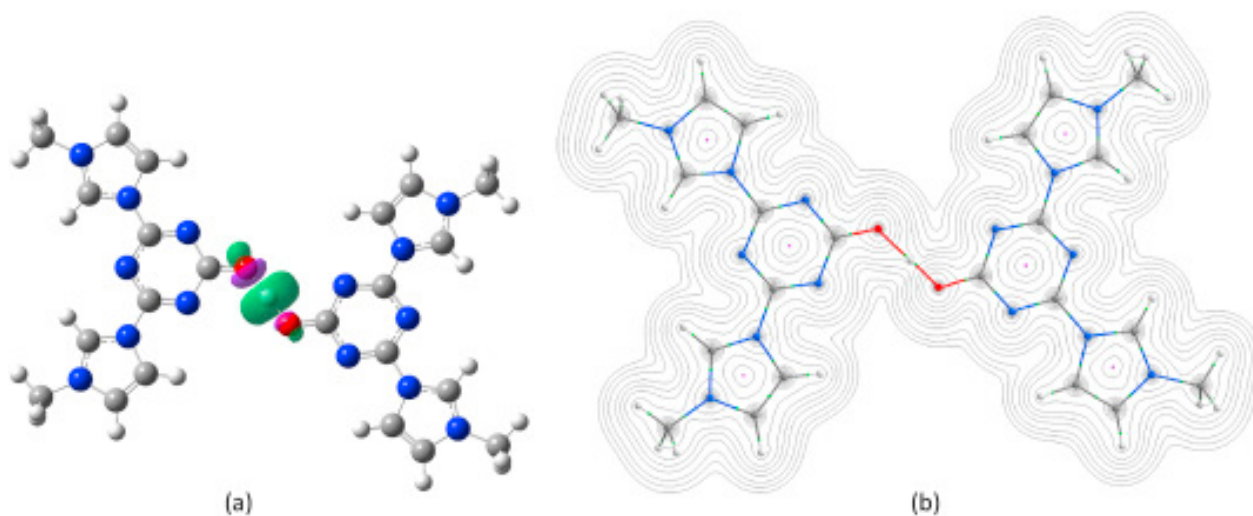


Fig. 3. (a) Calculated NBO stabilization interaction between the hydroxyl and alkoxy moiety within **4**. (b) QTAIM results of **4**, including electron density maps. BCPs are marked as small green spheres and RCPs as magenta ones. Colour code for atoms (online version): C (grey), N (blue), O (red), H (white).

4. Conclusions

This work presented the synthesis and characterization of a unique triazine-functionalized imidazolium hexafluorophosphate salt. The prepared salt is characterized by solution and solid state techniques including X-ray diffraction, which revealed that the structure comprises two identical cationic triazine moieties linked by positively polarized hydrogen between negatively polarized oxygens. DFT methods were used complementary to gain additional insight in the molecular structure and bonding of the hydrogen-bonded dimer.

Acknowledgements

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