



Supramolecular aggregation in new crystals with nonlinear optical properties: 2-aminophenol-HClO₄, 3-aminophenol-HClO₄ and 4-aminophenol-HClO₄

Jan Janczak^{a,*}, Genivaldo Julio Perpétuo^b

^aInstitute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O.Box 1410, 50-950 Wrocław, Poland

^bDepartamento de Física, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto, MG, Brazil

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ABSTRACT

Three new hybrid crystals of 2-aminophenol-HClO₄ (2-AP-HClO₄, **1**), 3-aminophenol-HClO₄ (3-AP-HClO₄, **2**) and 4-aminophenol-HClO₄ (4-AP-HClO₄, **3**) were obtained and their crystal structures determined. The **1** crystallises in centrosymmetric space group *C2/c* of monoclinic system while the other two (**2** and **3**) crystallise in the non-centro symmetric space group *P2₁* and *P2₁2₁2₁*, respectively. The oppositely charged units of the crystals, i.e. positively charged 2-APH⁺, 3-APH⁺ and 4-APH⁺ and ClO₄⁻, interact via weak N⁺–H···O and O–H···O hydrogen bonds forming 3D-supramolecular network. Relative to KDP the SHG efficiencies are 0.62 for **2** and 0.33 for **3**, measured at 1064 nm using the Kurtz–Perry method.

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1. Introduction

In recent years the studies on the self-assembly of organic and inorganic molecules in the solid state have become intense research activity due to their physical and chemical properties as well as due to their applications [1–5]. Crystal engineering utilises molecules that can form multiple interactions with the neighbours [6–8]. Many different types of hydrogen bonds, N–H···N, N–H···O, O–H···N and O–H···O, are the main key for organisation of molecules in solid, especially the molecules containing complementary arrays of hydrogen bonding sites [9–14].

A great attention has been devoted to obtaining new molecular materials for nonlinear optics [15–18]. One of the methods is based on the acid–base hydrogen bond interactions and molecular recognition [19–23]. These molecular crystals are built up of an inorganic/organic acids and organic base. The acid part of the molecular crystal is responsible for favourable chemical and mechanical properties, due to the directional and strong hydrogen bond interactions, while the organic part due to its relatively high hyperpolarisability is mainly responsible for the nonlinear optical properties of the crystals [24,25]. In this approach the individual

molecules are treated as independent units and the bulk properties can be thought of as being built up of the individual molecules with the corresponding properties [26].

In building acid–base hybrid crystals, it is interesting to note that perchloric acid forms molecular crystals with different organic bases that exhibit nonlinear optical properties [27]. The present work describes three hybrid crystals formed by perchloric acid with 2-aminophenol, 3-aminophenol and 4-aminophenol.

2. Experimental

2.1. Preparation of the crystals

All materials were commercially available (Aldrich) and used as received. Aqueous solutions of perchloric acid and the respective aminophenol (in stoichiometric proportions) were prepared and left to react at 360–370 K. When the solutions became homogeneous, they were cooled to the ambient temperature. After several days the crystals of the 1:1 complex were obtained by slow evaporation. Elemental analyses were carried out with a Perkin-Elmer 2400 elemental analyser. Infrared spectra were recorded on a Bruker IFS-88 spectrometer at a resolution of 2 cm⁻¹ using samples in Nujol. Elemental analysis and IR spectra confirm the chemical formulae of the title compounds.

* Corresponding author. Fax: +48 71 344 1029.

E-mail address: jjanczak@int.pan.wroc.pl (J. Janczak).

Table 1
Crystallographic data and structure refinement parameters.

Compound	1	2	3
Formula	C ₆ H ₈ NO·ClO ₄	C ₆ H ₈ NO·ClO ₄	C ₆ H ₈ NO·ClO ₄
Molecular weight	209.58	209.58	209.58
Temperature [K]	295	295	295
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	C2/c	P2 ₁	P2 ₁ 2 ₁ 2 ₁
a (Å)	20.400(3)	7.309(2)	7.230(1)
b (Å)	11.666(2)	6.303(1)	7.327(1)
c (Å)	7.685(2)	9.395(2)	16.686(3)
β (°)	104.34(1)	107.78(1)	
V (Å ³)	1771.9(6)	412.14(16)	883.9(2)
Z	8	2	4
D _{calc} [g cm ⁻³]	1.57	1.685	1.57
D _{obs} [g cm ⁻³]	1.571	1.689	1.575
μ (mm ⁻¹)	0.420	0.450	0.423
Crystal size (mm ³)	0.42 × 0.30 × 0.22	0.40 × 0.28 × 0.22	0.36 × 0.30 × 0.22
Total/unique/observed reflections (R _{int})	9764/1974/1588 (0.010)	5588/1978/1797 (0.011)	11791/2129/1771 (0.019)
R [F ² > 2σ(F ²)] ^a	0.025	0.020	0.036
wR [F ² all reffs]	0.062	0.047	0.099
S	1.002	1.001	1.010
Flack parameter		0.07(4)	0.09(9)
Δρ _{max} , Δρ _{min} (e Å ⁻³)	+0.176, -0.123	+0.162, -0.198	+0.196, -0.213

^a $w = 1/[\sigma^2(F_o^2) + (0.00281P)^2 + 0.5027P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 0.012P]$ for **2** and $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.05P]$ for **3** where $P = (F_o^2 + 2F_c^2)/3$.

2.2. Single crystal X-ray crystallography

Suitable single crystals of 2-aminophenol-HClO₄ (**1**), 3-aminophenol-HClO₄ (**2**) and 4-aminophenol-HClO₄ (**3**) were used for data collection on a four-circle KUMA KM4 diffractometer equipped with two-dimensional CCD area detector. The graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) and the ω -scan technique ($\Delta\omega = 1^\circ$) were used for data collection. Data collection and reduction along with absorption correction were performed using CrysAlis software package [28]. The structures were solved by direct methods using SHELXS-97 giving positions of almost all non-hydrogen atoms. The remaining atoms were located from subsequent difference Fourier syntheses. The structures were refined using SHELXL-97 [29] with the anisotropic thermal displacement parameters. Hydrogen atoms of the aromatic ring were located from the difference Fourier maps, but in the final refinement the positions of all hydrogen atoms were constrained: thermal parameters and distances. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Selected geometrical parameters are listed in Table 2.

Table 2
Geometric parameters (bond lengths in Å, bond angles in °).

	Compound 1	Compound 2	Compound 3
Cl1–O1	1.4135(11)	1.4171(10)	1.4211(14)
Cl1–O2	1.4271(11)	1.4179(9)	1.4178(19)
Cl1–O3	1.4329(11)	1.4341(11)	1.4204(17)
Cl1–O4	1.4339(11)	1.4354(12)	1.4246(14)
C1–C6	1.380(2)	1.3756(16)	1.356(3)
C1–C2	1.3833(17)	1.3859(17)	1.368(2)
C2–C3	1.3738(18)	1.3705(18)	1.371(3)
C3–C4	1.380(2)	1.3705(19)	1.368(3)
C4–C5	1.384(2)	1.370(2)	1.354(3)
C5–C6	1.374(2)	1.3725(17)	1.383(3)
O5–C _{ring}	1.3655(16)	1.3566(15)	1.376(2)
N1–C _{ring}	1.4718(16)	1.4603(14)	1.4638(19)
O1–Cl1–O2	109.90(8)	110.03(6)	111.17(13)
O1–Cl1–O3	109.56(8)	108.43(7)	111.12(12)
O1–Cl1–O4	107.56(7)	109.28(8)	107.59(10)
O2–Cl1–O3	110.70(7)	109.46(6)	110.00(15)
O3–Cl1–O4	110.58(8)	109.35(8)	108.19(13)

2.3. Second harmonic generation (SHG)

Second harmonic generation properties were measured for the solid state samples at the fundamental wavelength (1064 nm) of a Q-switched Nd:YAG laser using the modified Kurtz–Perry method [30].

3. Results and discussion

3.1. Crystal structure of 2-AP-HClO₄ (**1**)

The asymmetric unit of **1** with the atomic labelling scheme is illustrated in Fig. 1a. The C–N bond linking the protonated amine group is longer by ~ 0.05 Å than that in neutral 2-aminophenol [31]. The C–OH and C–C bonds within the aromatic ring are comparable to that found in the crystal of a neutral 2-aminophenol.

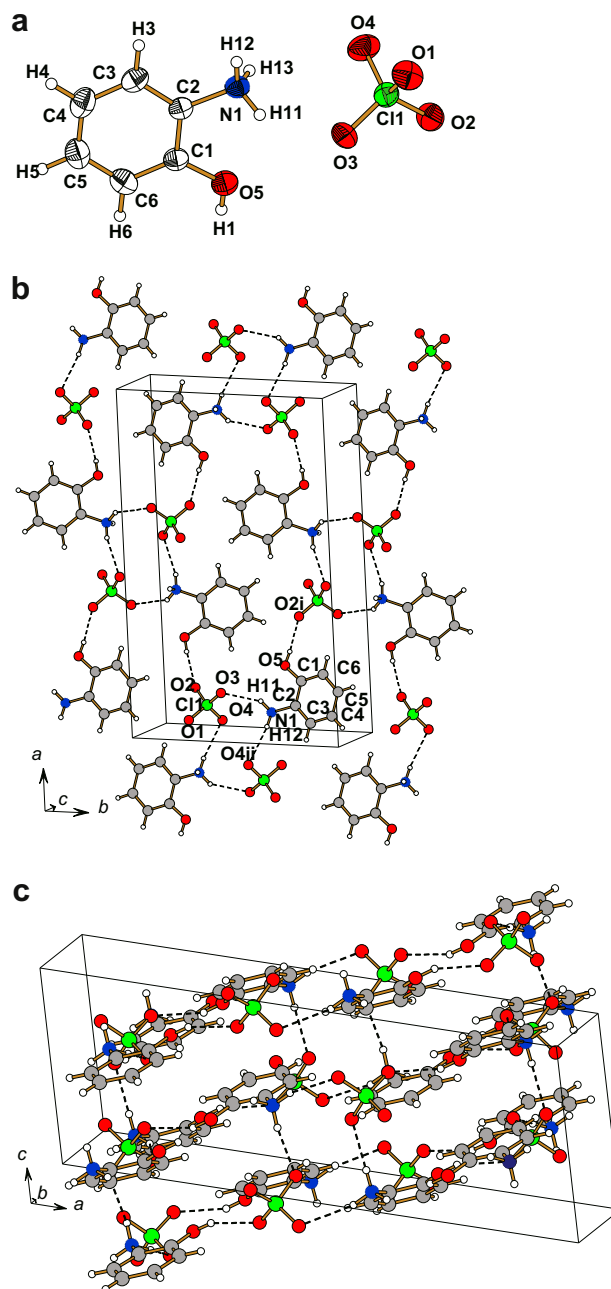
**Fig. 1.** View of the asymmetric unit of **1** (a), 2D-layer of hydrogen-bonded *o*-AFH⁺ and ClO₄⁻ (b) and the 2D-layers (c).

Table 3
Geometry of the hydrogen bonds (Å, °).

Compound 1				
A–H...D	d(A–H)	d(H...D)	d(A...D)	<(AHD)
N1–H11...O3	0.89	2.24	3.0038(16)	144
O5–H1...O2 ⁱ	0.82	2.05	2.8245(16)	158
N1–H12...O4 ⁱⁱ	0.89	2.32	3.1762(18)	160
N1–H13...O1 ⁱⁱⁱ	0.89	2.10	2.9339(17)	156
Symmetry code: $i = -x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; $ii = -x, -y + 1, -z$; $iii = x, -y + 1, z + \frac{1}{2}$.				
Compound 2				
O5–H5...O1 ⁱ	0.88(2)	1.938(19)	2.7943(14)	163(2)
O5–H5...O2 ⁱ	0.88(2)	2.557(19)	3.0008(13)	112(1)
N1–H11...O4	0.89	2.28	3.0088(17)	140
N1–H12...O3 ⁱⁱ	0.89	2.09	2.957(2)	165
N1–H13...O5 ⁱⁱⁱ	0.89	2.07	2.8803(16)	150
N1–H13...O4 ^{iv}	0.89	2.50	3.1288(14)	128
Symmetry code: $i = x, y - 1, z + 1$; $ii = x, y - 1, z$; $iii = -x + 1, y + \frac{1}{2}, -z + 1$; $iv = -x + 1, y - \frac{1}{2}, -z$.				
Compound 3				
N1–H11...O1 ⁱ	0.89	2.05	2.881(2)	157
N1–H12...O3	0.89	2.12	2.862(2)	139
N1–H13...O4 ⁱⁱ	0.89	2.10	2.951(2)	160
O5–H50...O2 ⁱⁱⁱ	0.82	2.30	3.066(2)	155
O5–H50...O4 ^{iv}	0.82	2.37	2.865(2)	120
Symmetry code: $i = x - \frac{1}{2}, -y + \frac{1}{2}, -z$; $ii = x - 1, y, z$; $iii = -x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; $iv = -x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.				

The perchlorate anion, ClO₄⁻, exhibits slightly distorted tetrahedral geometry with the Cl–O distances ranging from 1.4135(11) to 1.4354(12) Å. Each 2-APH⁺ cation is linked by three relatively weak N⁺–H...O and one O–H...O hydrogen bonds to the four perchlorate anions (Table 3). Two 2-APH⁺ cations and two ClO₄⁻ anions related by an inversion center are joined together via two pairs of N⁺–H...O

hydrogen bonds forming dimeric [2-APH⁺·ClO₄⁻]₂ units. These units interact to each other by the hydrogen bonds between the phenolic hydroxyl group (donor) and one of oxygen atom (O₂) of perchlorate anions forming infinite 2D-layers (Fig. 1b). These layers are almost parallel to (10–1) crystallographic plane (Fig. 1c). The neighbouring layers interact via N⁺–H...O hydrogen bonds forming a 3D supramolecular network.

3.2. Crystal structure of 3-AP-HClO₄ (2)

The asymmetric unit of **2** with the atomic labelling scheme illustrated in Fig. 2a. The 3-APH⁺ cations related by a screw twofold axis interact by a pair of N⁺–H...O hydrogen bonds between the protonated amine group as a donor and phenolic hydroxyl group as an acceptor forming chains running along the *b*-axis (Fig. 2b). The chains interact via N⁺–H...O hydrogen bonds with the perchlorate anions forming double layers. In the crystal the double layers are running parallel to (100) crystallographic plane (Fig. 2c). The double layers interact only by the van der Waals forces. In the crystal no π–π interactions between the aromatic rings are observed, since the closest neighbouring rings are not parallel, but inclined by an angle of 44.4(1)°. The C–N bond linking the protonated amine group with a distance of 1.4604(14) Å is longer than that in the crystal of neutral 3-aminophenol (1.424(2) Å). The C–OH and C–C bond lengths are comparable to that found in the crystal of neutral 3-aminophenol [32].

3.3. Crystal structure of 4-AP-HClO₄ (3)

The asymmetric unit of **2** with the atomic labelling scheme is illustrated in Fig. 3a. The C–N bond linking the protonated amine

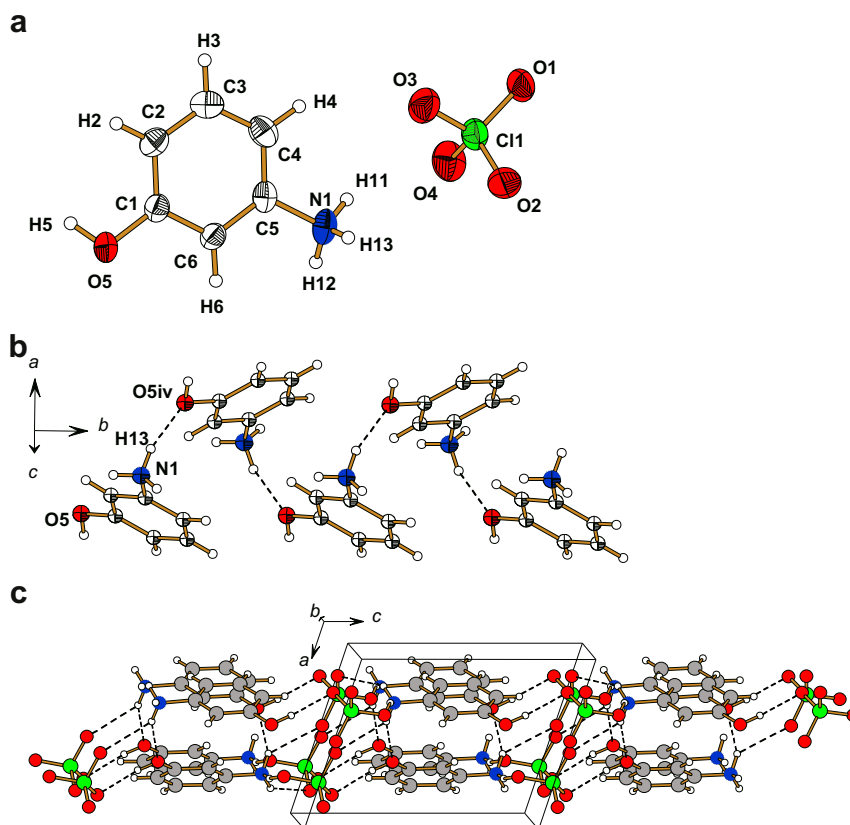


Fig. 2. The asymmetric unit of **2** (a), N–H...O hydrogen-bonded chain of *o*-APH⁺ cations (b) and the arrangement of **2** in the unit cell showing the double layers (c).

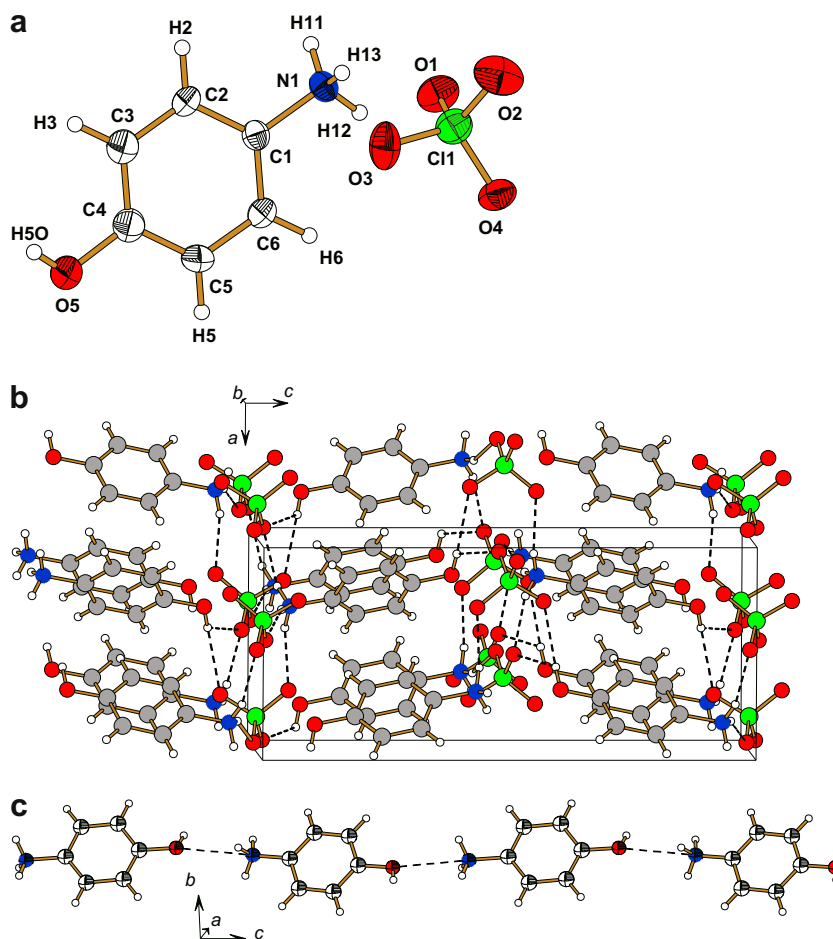


Fig. 3. The asymmetric unit of **3** (a), packing of **3** in the unit cell showing N–H...O and O–H...O hydrogen bonds (b) and 1D arrangement of *p*-AFH⁺ cations in chain (c).

group is longer by ~ 0.03 Å than that found in the crystal of neutral 4-aminophenol [33]. The C–OH bond and C–C bonds within the aromatic ring are comparable to that found in the crystal of a neutral 4-aminophenol. The protonated amine group NH_3^+ interacts via $\text{N}^+ \cdots \text{H} \cdots \text{O}$ hydrogen bonds with three different perchlorate anions. The phenolic hydroxyl group as a donor is involved in the bifurcated hydrogen bonds with two perchlorate anions as acceptors (Table 3). The oppositely charged units, i.e. 4-APH⁺ and ClO_4^- , interact to each other forming the hydrogen bonded 3D-supramolecular network (Fig. 3b). It is interesting to note that the 4-APH⁺ cations related by a screw twofold axis are forming 1D-polymer along the crystallographic *c* axis (Fig. 3c). The oppositely polarised groups of 4-APH⁺ (OH and NH_3^+) may interact electrostatically since the distance between the O and N atoms is relatively short ($\text{N1} \cdots \text{O5}^\#$ 2.898(2) Å # $-x + 0.5, -y + 1, z - 0.5$).

3.4. Second harmonic generation (SHG) properties

The second harmonic generation properties were measured on crystalline samples that were irradiated at 1064 nm and the second harmonic beam power diffused by the samples at 532 nm were measured as a function of the fundamental beam power. The SHG efficiency relative to KDP was found to be 0.62 for **2** and 0.33 for **3**. The sample of **1** was optically inactive, since this 2-aminophenol– HClO_4 hybrid complex crystallises in the centrosymmetric $\text{C2}/c$ space group.

3.5. Infrared spectroscopy

The FT-IR spectra of the *o*-, *m*- and *p*-ammoniumphenol perchlorate complexes were recorded at room temperature (Fig. 4a,b and c). In all spectra there are observed the bands for perchlorate anion. For an isolated ClO_4^- group with T_d symmetry nine normal modes manifested as four bands (ν_1, ν_2, ν_3 and ν_4) can be expected. According to the literature data [34] the frequencies are: ν_3 (F_2) = 1119 cm^{-1} (antisymmetric stretching), ν_1 (A_1) = 928 cm^{-1} (symmetric stretching), ν_4 (F_2) = 625 cm^{-1} (in-plane deformation) and ν_2 (E) = 459 cm^{-1} (out-of-plane deformation). The similarity of spectroscopic behaviour between tetrahedral ClO_4^- and SO_4^{2-} was noted [35,36]. There is no band observed in the spectra of **1**, **2** and **3** at about 890 cm^{-1} (Cl–O_H stretching). This corroborates the slightly distorted conformation of ClO_4^- from ideal tetrahedral symmetry with Cl–O distances ranging from 1.4135(11)–1.4354(12) Å (see Table 2). Due to the lower symmetry of ClO_4^- from T_d , the splitting can be observed for the doubly degenerate ν_2 and triply degenerate ν_3 and ν_4 modes. The assignment of the bands corresponding to particular modes of ClO_4^- anion is given in Table 4. Besides the characteristic bands of ClO_4^- anion, the majority of the bands observed in the infrared spectra of the title compounds belong to aromatic ring modes of *o*-AF, *m*-AF and *p*-AF isomers. Additionally, only some of the bands may be assigned to the NH_3^+ and OH groups of ammoniumphenol isomers, as well as for the $\text{N}^+ \cdots \text{H} \cdots \text{O}$ and O–H...O types of hydrogen bonds. For the assignment of the phenyl ring modes the classical works of Herzberg [37] and Miller [38] are

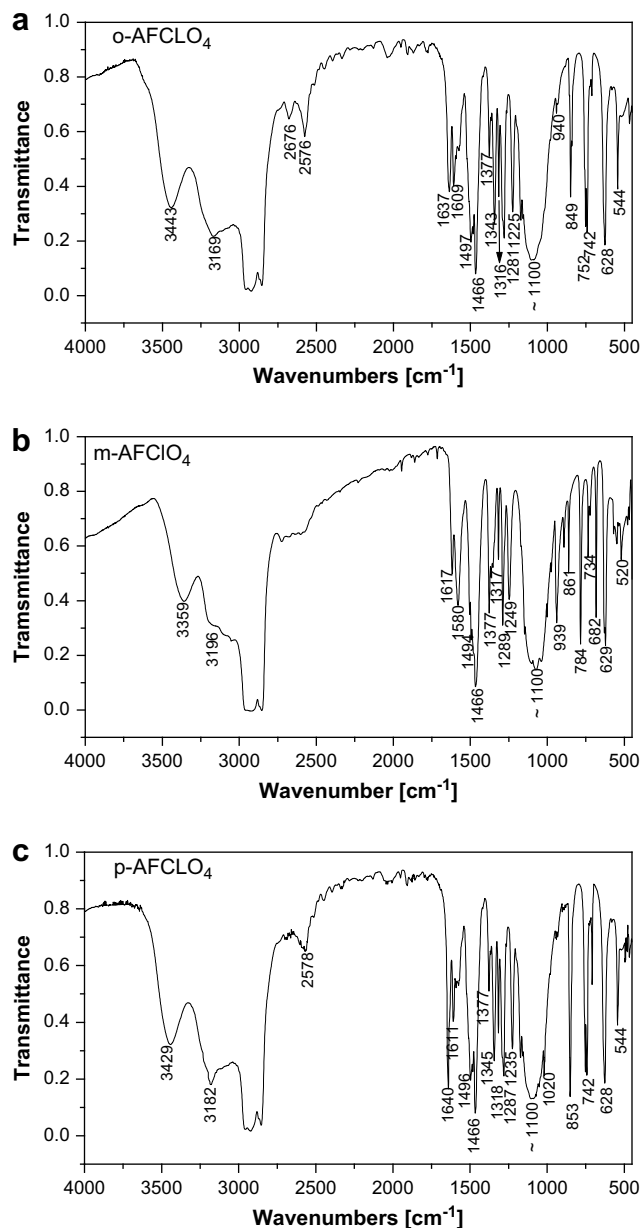


Fig. 4. Room temperature FT-IR spectra of *o*-ammoniumphenol perchlorate (a), *m*-ammoniumphenol perchlorate (b) and *p*-ammoniumphenol perchlorate (c).

helpful. The sharp strong bands at ~ 3380 and ~ 3300 cm^{-1} for *o*-AF and *m*-AF and at ~ 3355 and ~ 3285 cm^{-1} for *p*-AF in the spectra of aminophenol isomers corresponding to amine group (i.e. antisymmetric and symmetric stretching) are broadened and shifted in the spectra of perchlorate salt due to intermolecular interactions through hydrogen bonds. According to the X-ray data, all three protons of NH_3^+ group are involved in weak hydrogen-bonding interactions (Table 3). A broad and intense absorption in the range 3600 – 2700 cm^{-1} can be assigned to antisymmetric and symmetric stretching vibrations of NH_3^+ and OH groups interacting through hydrogen bonds with oxygen atoms of perchlorate anions. The several bands at ~ 150 , ~ 1318 , ~ 1289 and ~ 1166 cm^{-1} which originate from in-plane deformations of the hydrogen bonds are observed in the spectra of **1**, **2** and **3**. The strong infrared band at about 744 cm^{-1} can be assigned to the in-plane ring deformations. The very broad band at ~ 1100 cm^{-1} is characteristic for all spectra

Table 4

Wavenumber (cm^{-1}) and relative intensities^a of the bands in infrared spectra of **1**, **2** and **3**.

1 (<i>o</i> -AFH ⁺)ClO ₄ ⁻	2 (<i>m</i> -AFH ⁺)ClO ₄ ⁻	3 (<i>p</i> sAFH ⁺)ClO ₄ ⁻	Assignments
3443sb	3359sb	3429sb	NH ₃ ⁺ asym stretch
3169sb	3196sb	3182sb	NH ₃ ⁺ sym stretch
2676w	2668w	2681w	
2576w	2574w	2578w	
1637m	1617m	1640s	
1609m		1611m	Ring stretch
1575m	1580m	1582sh	NH ₃ ⁺ asym def; N–H...O in plane def
1508sh	1510sh	1510sh	NH ₃ ⁺ asym def
1497s	1494s	1496s	Ring stretch
1466s	1466s	1466s	Nujol
1418sh	1420sh	1418sh	
1377m	1377m	1377m	Nujol
1343s	1344sh	1345s	
1316m	1317m	1318m	N–H...O and O–H...O in plane def
1281s	1289s	1287s	N–H...O and O–H...O in plane def
1225m	1249m	1235m	N–H...O and O–H...O in plane def
1195sh	1196sh	1195sh	N–H...O and O–H...O in plane def
1166sb	1168sh	1167sh	N–H...O and O–H...O in plane def
1148sh	1147sh	1147sh	ClO ₄ ⁻ asym stretch, ν_3 (F ₂)
1100sb	1100sb	1100sb	ClO ₄ ⁻ asym stretch, ν_3 (F ₂)
1047sh	1039sh	1042sh	ClO ₄ ⁻ asym stretch, ν_3 (F ₂)
1016sh	1018m	1020s	6(A ₁) mode of phenyl ring
1000sh	999sh	1000sh	ring C=C sym stretch
940w	939s	938w	ClO ₄ ⁻ sym stretch, ν_1 (A ₁)
849s	861m	853s	
752s	784s		In plane ring def
742s	734m	742s	In plane ring def
628s	629s	628s	ClO ₄ ⁻ asym def, ν_4 (F ₂)
616sh	619sh	617sh	ClO ₄ ⁻ asym def, ν_4 (F ₂)
544m	541w	544m	ClO ₄ ⁻ sym def, ν_2 (E ₂)
455w	460sh	470m	ClO ₄ ⁻ sym def, ν_2 (E ₂)

^a Abbreviations: s – strong, m – medium, w – weak, sh – shoulder, b – broad.

and are assigned to the asymmetric stretching ν_3 mode that splits in three overlapped bands (~ 1147 , ~ 1100 and ~ 1170 cm^{-1}).

4. Conclusion

The hybrid acid–base crystals of three isomers of aminophenol with perchloric acid have been prepared and their crystal structures determined. Protonation of the amine group leads to elongation of the C_{ar}–NH₃ bond by ~ 0.05 Å in relation to the neutral molecule. The acid–base hydrogen bonding interactions lead to a self-assembly organisation forming the 3D supramolecular architecture. Two crystals of perchlorate salts of 3-AP and 4-AP isomers exhibit interesting nonlinear properties. The perchlorate salt of 2-AP isomer is optically inactive since it crystallises in the centrosymmetric space group. The organic parts of perchlorate salts, i.e. 3-APH⁺ and 4-APH⁺, are mainly responsible for these NLO properties due to the presence of both electron donor and electron acceptor groups in the π -electron system. The influence of the hydrogen bonding on the enhancement of the hyperpolarisability of the cationic parts of the crystals as well as the contribution of vibrational hyperpolarisability to the nonlinear optical properties should be taken into account.

Supplementary material

The X-ray crystallographic data for the structures reported in this paper have been deposited at the CCDC as supplementary data, CCDC Nos. 705365, 705366 and 705367. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

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