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X-ray, vibrational spectra and quantum chemical studies on a new semiorganic crystal: 4-Chloroanilinium perchlorate

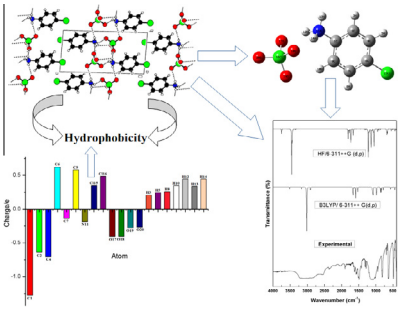
R. Anitha [a,1], S. Athimoolam [b,*], M. Gunasekaran [a,1], K. Anitha [c]

[a] Department of Physics, Regional Centre, Anna University Tirunelveli Region, Tirunelveli 627 007, India
[b] Department of Physics, University College of Engineering, Nagercoil, Anna University, Nagercoil 629 004, India
[c] Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

HIGHLIGHTS

- 4CAP was crystallized by the slow evaporation technique.
- The complete vibrational assignment and spectroscopic analysis of 4CAP have been carried out.
- Mulliken charge analysis was investigated.
- Nonlinear optical properties (NLO), natural bond orbital (NBO) and HOMO/LUMO analysis were analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

A new semi-organic material 4-chloroanilinium perchlorate was synthesized and grown as a single crystal by slow evaporation solution growth technique. A good X-ray quality single crystal was selected from the grown crops and used for the single crystal diffraction studies. The asymmetric part of the unit cell contains a 4-chloroanilinium cation and a perchlorate anion. The protonation on the N site of the chloroaniline is confirmed from the CN bond distance and the deprotonation on perchloric acid is confirmed from ClO bond geometry. The molecular aggregations are stabilized through intricate three dimensional hydrogen bonding network formed by the classical NH···O hydrogen bonds. It form two infinite chains running along the *b*-axis of the unit cell which are cross-linked through another NH···O bond leading to alternate ring $R_4^4(12)$ motifs. These ring and chain motifs lead to alternate hydrophilic and hydrophobic layers along *c*-axis of the unit cell. The presence of different functional groups and the nature of their vibrations were identified in experimental vibrational studies through Infra-Red and Raman measurements in the range of 4000–400 cm^{-1}. The optimized molecular structure, vibrational mode, computed spectra, molecular properties and NBO analysis of the 4-chloroanilinium perchlorate were found out by quantum chemical calculations with HF and DFT/B3LYP methods invoking 6-311++G(d,p) basis sets. Computed geometrical parameters and harmonic frequencies of fundamental, combination and overtone transitions were found in satisfactory agreement with the experimental data. The electronic properties such as HOMO and LUMO energies were carried out.

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Introduction

Aniline and its related structures are widely studied because of its importance in many pharmaceutical, electro-optical and several other social applications like production of dyes and pesticides. In

* Corresponding author. Tel.: +91 9787100212; fax: +91 4652 260511.
E-mail address: athi81s@yahoo.co.in (S. Athimoolam).
[1] Present address: Department of Physics, DMI Engineering College, Aralvaimozhi 627105, India.

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pharmaceutical industry, it is used as a precursor to produce antimicrobial and bacteriocide chlorhexidine and is used in the manufacture of pesticides, including pyraclostrobin, anilofos, monolinuron and chlorphthalim. Also aniline is an important raw material for many industrial uses such as oil paints, rubber and plastics. It has been widely studied for its use in electrical conduction, electroluminescence, rechargeable batteries and anti corrosion applications [1–3]. In most of the cases, the applications are ensued due to the intermolecular interactions especially hydrogen bonds which has its importance in the areas of molecular recognition, crystal engineering research and supramolecular chemistry. Understanding of these non-covalent interactions has proved to be the most valuable because of its strength and directional properties [4]. The strength and directionality of hydrogen bonding interactions is responsible for solid state formation and other physical properties of the system [5].

4-Chloroaniline is used as an intermediate in the production of several urea herbicides and insecticides (e.g., monuron, diflubenzuron), azo dyes, pigments, pharmaceutical and cosmetic products. It is a precursor to the widely used antimicrobial and bacteriocide chlorhexidine and is used in the manufacture of pesticides, including pyraclostrobin, anilofos, monolinuron and chlorphthalim [6]. Also we continuously seek to identify hydrogen bond enriched assemblies by means of a single efficient organic hydrogen bonding synthon. Substituted anilines are good candidates for this type of supramolecular synthon as it is have both donor and acceptor sites, viz., nitrogen and chlorine atoms. Crystallographic studies on the protonated chloroaniline complexes are known for last two decades. From Cambridge Structural Database (CSD ver. 5.35), it is observed that there are 28 protonated chloroaniline (chloroanilinium) structures reported so far [7]. In all the cases, the hydrogen of the organic/inorganic acid is liberated and attached to the —NH_2 group of the chloroaniline and it become chloroanilinium cation and the corresponding counterpart become deprotonated anion. The perchlorate salt of the 4-chloroaniline with the crown solvent was crystallized and already reported [8]. The present work was attempted the new 4-chloroanilinium perchlorate of a semi-organic crystal without solvent. Though the single crystal XRD clearly predicts the molecular structure and packing tendency of the molecule in the solid crystalline state. The spectral measurements given an account of strength of the intermolecular interactions by means of shifting of wavenumbers and the intensity of the peaks. Further, the molecular geometry obtained from the crystallographic data is a well-suited input for the quantum chemical calculations. By which, we can optimize the molecule in different environment and the corresponding vibrational modes can be calculated. Further, the bond analyses and band gap values can be inferred from this study. Hence, a combined crystallographic, spectroscopic and quantum chemical calculations were attempted on new semi-organic crystal 4-chloroanilinium perchlorate and the results are summarized.

Experimental

Preparation

Crystals of 4-chloroanilinium perchlorate (4CAP) were synthesized from an aqueous mixture of 4-chloroaniline and perchloric acid with a stoichiometric ratio of 1:1 at room temperature by slow evaporation. After a week period, block type colourless crystals of 4CAP were obtained. The quality of the crystals are improved by recrystallization.

Density measurement

The density of the crystal was measured by sink and swim method (flotation technique) using a liquid mixture of carbon tetrachloride and bromoform. Initially, carbon tetrachloride of 10 ml was taken in a test tube and a good quality three dimensional crystal was placed on it. Due to the more density than the liquid, the crystal started to sink. Then, drops of Bromoform was added drop-by-drop with continuous agitation to get uniform density over the liquid. When the density of the crystal and the liquid matches the crystal start to levitate on the middle of the test tube. Then, the density of the liquid was found with specific gravity bottle by the concept of relative density. Thus, the density of the crystal was founded to be 1.65 (2) Mg m^{-3}.

Single crystal XRD studies

The entire crystallographic calculations of 4CAP were done with Enraf Nonius MACH-3 CAD4 sealed-tube diffractometer (graphite-monochromated, Mo Kα = 0.71073 Å) using ω–2θ scan technique at room temperature. A good X-ray quality single crystal of approximate dimension of 0.21 × 0.18 × 0.16 mm^3 was selected from the grown crystals and used for the single crystal X-ray diffraction studies. Initially, the obtained cell parameters were checked with the Cambridge Structural Database for the confirmation of the new semi-organic crystal [7]. Consequently, the full data collection of the crystal was carried out. The cell refinement and data reduction was done with XCAD4 software [9]. The structure was solved and refined with the SHELXTL/PC programme [10]. The reliability index (*R*-factor) for $F^2 > 2\sigma(F^2)$ is found to be 6.8%, which confirms the convergence of the reliable structure. The crystal data, details of data collection and structure refinement are given in Table 1.

All the H atoms were discernible in the difference electron density map. Nevertheless, the aryl H atoms were constrained and refined in the riding atom approximation: CH = 0.93 Å and U_{iso}(-H) = 1.2U_{eq}(C). The other H atoms, which are involved in the NH···O hydrogen bonds were located from electronic density map and refined isotropically. Atomic coordinates and equivalent displacement parameters are listed in Table 2.

Parameters in CIF format are available as Electronic Supplementary Publication from Cambridge Structural Data Centre (CCDC 998662). Graphical molecular illustrations were done with ORTEP3 for windows [11] and mercury [12] packages. Fig. 1 shows the

Table 1
Crystallographic data for 4CAP single crystal.

Compound name	4-Chloroanilinium perchlorate
Empirical formula	$(C_6H_7Cl\ N)^+\cdot(ClO_4)^-$
Formula weight	228.03
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 5.0431(6) Å; α = 92.965(13)°
	b = 6.9623(8) Å; β = 91.371(11)°
	c = 13.6035(9) Å; γ = 104.865(9)°
Volume	460.69(8) $Å^3$
Z, calculated density	2, 1.644 Mg m^{-3}
Absorption coefficient	0.685 mm^{-1}
F(000)	232
Theta range for data collection	3.00–24.97°
Limiting indices	$-1 \leqslant h \leqslant 5$, $-8 \leqslant k \leqslant 8$, $-16 \leqslant l \leqslant 16$
Reflections collected/unique	2422/1596 [R(int) = 0.0447]
Completeness to theta = 24.97	99.90%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1596/0/131
Goodness-of-fit on F^2	1.108
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0679, $wR2$ = 0.1672
R indices (all data)	$R1$ = 0.0773, $wR2$ = 0.1760
Extinction coefficient	0.033(14)
Largest diff. peak and hole	0.822 and −0.540 e $Å^{-3}$
CCDC no.	CCDC 998,662

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