

Short hydrogen bonds in a new salt of pyromellitic acid: An experimental charge density investigation

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ABSTRACT

An analysis of intra- and intermolecular short hydrogen bonds in a new salt of nicotinic acid (3-pyridinecarboxylic acid), Nic, and pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid), H_4Pm , with formula $(HNic)_2(H_2Pm)$, **1**, has been carried out by single-crystal X-ray diffraction method at 120 K. The experimental charge density has been performed using multipolar functions and analyzed by Quantum Theory of Atoms in Molecules, which gave evidence for the partly covalent character of those interactions.

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1. Introduction

Hydrogen bonding has attracted much attention as a fundamental element of chemical structure and reactivity in biological systems. It is the key to understanding the formation of higher order structures of peptides and nucleic acids and some biochemical processes, particularly the enzymes catalyzed [1]. On the one hand, it is a relatively strong directional interaction leading to stable supramolecular structures. On the other hand, it is an active site for the initiation of chemical reactions due to dynamic nature of the hydrogen atom.

Despite the increasing interest, there are many unresolved problems about the nature of hydrogen bonds. In particular, current controversies are focused on $O-H\cdots O$ short hydrogen bonds (SHB), whose $O\cdots O$ lengths are shorter than ≈ 2.50 Å [2]. These interactions have been suggested to have covalent character based on diverse experimental and theoretical techniques, including infrared and NMR spectroscopies and X-ray and neutron diffraction [3]. Gilli and co-workers (see [4] for a recent summary) proposed a resonance between covalent structures (e.g., $O-H\cdots O \leftrightarrow O\cdots H-O$). In this model all SHB could be referred as (a) negative charge-assisted H-bond, $[-O-H\cdots O]^-$; (b) positive charge-assisted H-bond, $[=O-H\cdots O]^+$; (c) double charge-assisted H-bond $[=^+O-H\cdots O^-]$ or (d) resonance-assisted H-bond, $[-O-H\cdots O=]$ where the two oxygen atoms are connected by a π -conjugated system. However,

some authors have opposed counterexamples to this view based both on experimental and on theoretical results [5,6].

Polycarboxylic acids are important systems to study $O-H\cdots O$ hydrogen bonds, in part, due to the possible formation of SHB. In particular, benzenepolycarboxylic acids are very interesting systems. These compounds are rigid, but with different values of dihedral angles between the plane of the carboxylic groups and the phenyl ring plane. Due to this, polycarboxylic acids as 1,2-benzenedicarboxylic acid, 1,2,4-benzenetricarboxylic acid and 1,2,4,5-benzenetetracarboxylic acid have been used to generate many compounds with uncommon multi-dimensional networks containing channels and cavities with various sizes and shapes [7–9]. 1,2,4,5-benzenetetracarboxylic acid, also known as pyromellitic acid (H_4Pm), can form different types of compounds by substitution of one to four hydrogen atoms. Acid salts of H_4Pm may present intramolecular SHB due to the proximity of carboxyl groups. Various single-crystal structures derived of this acid have been reported [10–14].

Throughout the last decades, with technical advances in X-ray crystallography, especially the introduction of CCD area detectors, it has become possible to collect accurate, high-resolution diffraction data for experimental charge-density in one or few days [15] rather than weeks or even months. Such improvements have made X-ray diffraction a unique tool for mapping the charge distribution in crystals [16]. The topological analysis using Quantum Theory of Atoms in Molecules (QTAIM) approach of Bader [17] has been central to understand the nature of bonding and non-bonding interactions because it is based in electron distribution rather than limited to the classical connectivity between atoms. In this sense, there has been increasing interest in the study of weak intra- and intermo-

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lecular interactions, especially hydrogen bonds, using these methods [18–20]. In the present work, hydrogen bonds have been analyzed in a new salt obtained from H₄Pm: bis(3-carboxypyridinium) 2,5-dicarboxybenzene-1,4-dicarboxylate, **1** (Scheme 1). The crystal structure of **1** has been examined and an experimental electron density study has been performed to investigate the intramolecular SHB and other H-bonds in more detail using QTAIM model.

2. Experimental section

2.1. Materials and instruments

All reagents were obtained from Sigma–Aldrich® and used as received without further purification. Thermogravimetric measurements (TG/DTG) were done using a Shimadzu TG-60 thermo balance. Samples were heated at 10 °C min⁻¹ from room temperature to 750 °C in dynamic air atmosphere, with a flow rate equal to 100 mL min⁻¹.

Fourier-transform Raman spectroscopy was carried out using a Bruker RFS 100 instrument and a Nd³⁺/YAG laser operating at 1064 nm in the near infrared with a CCD detector cooled with liquid N₂. Good signal-to-noise ratios were obtained from 512 scans and 100 mW of laser power at a spectral resolution of 4 cm⁻¹. The spectrum was obtained twice to show reproducibility and no changes in band positions and intensities were obtained. Infrared spectrum was obtained using a Bomem MB-102 spectrometer fitted with a CsI beam splitter, in the form of KBr disks and with a spectral resolution of 4 cm⁻¹. Good signal-to-noise ratios were obtained from the accumulation of 128 scans.

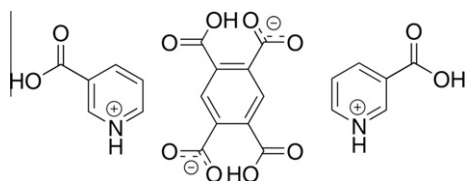
2.2. Synthesis

Aqueous solution of 2.0 mmol (246 mg) of 3-pyridinecarboxylic acid (nicotinic acid) were prepared and slowly added to an aqueous solution of 1.1 mmol (280 mg) of 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid). The resultant mixture was stored at room temperature. After few days, single-crystals of **1** were obtained. Anal. Calc. for C₂₂H₁₆N₂O₁₂: C, 52.80; H, 3.23; N, 5.60%. Found: C, 54.91; H, 3.05; N, 5.54%. ν(OH), 3447 (IV); ν(CH) + ν(NH), 3047 (IV, R); ν(C=O) + δ(OH), 1707 (IV, R); ν_{ring} + ν_{asym}(COO), 1598 (R); ν_{sym}(COO) + δ(OH), 1394 cm⁻¹ (R).

2.3. X-ray data collection and processing

The crystal structure of **1** (Fig. 1) was determined by single-crystal X-ray diffraction analysis at 120 K. Details of data collection and refinement procedures are given in Table 1. Measurements were carried out on an Xcalibur Atlas Gemini ultra diffractometer equipped with an Oxford Instruments Cryojet high temperature – low temperature device. Data collection, reduction and cell refinement were performed by CRYCALIS PRO programs [21].

A total of 1053 image frames were obtained using two different exposure times. The unit cell dimensions were determined by post-refinement of 87,821 reflections (2.1° < θ < 67.9°). An analytical absorption correction was applied using a multifaceted crystal



Scheme 1. Bis(3-carboxypyridinium) 2,5-dicarboxybenzene-1,4-dicarboxylate, **1**.

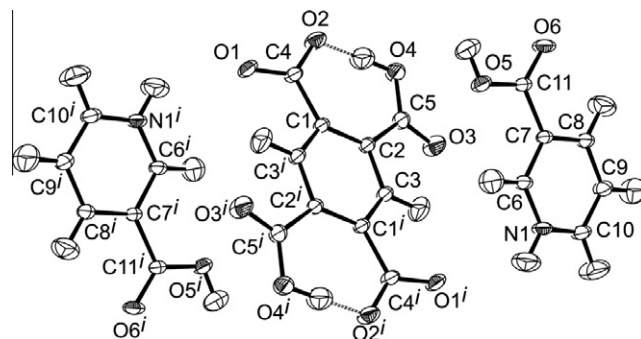


Fig. 1. Crystal structure of **1**. The label number for H-atoms is the same as for their attached heavy atom and is not displayed. Ellipsoids are drawn at 70% probability level. Symmetry code: (i) $-x + 1, -y + 1, -z$.

model based on expressions derived by Clark and Reid [22] as implemented in SCALE3 ABSPACK scaling algorithm [23]. A total of 319,860 reflections were collected with a mean redundancy of 17.3. The resulting data were merged using SORTAV [24,25] giving 18,457 independent data until resolution of $\sin(\theta_{max})/\lambda = 1.30 \text{ \AA}^{-1}$ ($\theta_{max} = 68.0^\circ$ for MoK α radiation).

2.4. Spherical refinement

The structure was solved by SHELXS-97 [26] and spherically refined on F^2 using all data by full-matrix least squares using SHELXL-97 [27]. These programs are implemented in WINGX package [28]. All non-H atoms were refined anisotropically. Aromatic H-atoms were placed in calculated positions and refined using a rigid model with an isotropic displacement parameter fixed at 1.2 times U_{eq} for the atom to which they are attached. Carboxyl H-atoms were located in difference Fourier map and refined isotropically. Displacement ellipsoid plots were obtained using ORTEP-3 for windows [29].

2.5. Multipole refinement

Multipole refinement was performed using XD2006 program suite [30] and the Hansen–Coppens formalism [31]. This formalism allows modeling of the deformation fraction of $\rho(\mathbf{r})$ using atom-centered multipole functions,

$$\rho_{\text{atom}}(\mathbf{r}) = \rho_{\text{core}}(\mathbf{r}) + P_v \kappa \rho_{\text{valence}}(\kappa \mathbf{r}) + \Delta \rho \quad (1)$$

in which

$$\Delta \rho = \sum_{l=0}^{l_{\text{max}}} \kappa' R_l(\kappa' \cdot \mathbf{r}) \cdot \sum_{m=0}^l P_{lm\pm} Y_{lm\pm}(\theta, \varphi)$$

The core and spherical valence density are composed of Hartree–Fock wavefunctions expanded by Slater-type basis function [32]. The valence shell is either contractible or expandable by the κ parameter. Single zeta orbitals with energy-optimized Slater exponents are taken for the deformation terms. Another contraction-expansion term, κ' , is also used. P_v and $P_{lm\pm}$ represent the population parameters for the valence and deformation density multipoles respectively. The angular functions $Y_{lm\pm}$ are real spherical harmonic functions, which are normalized for the electron density [33].

The function minimized in the least-squares procedure was $\Sigma w(|F_o| - K|F_c|)^2$, in which only those reflections with $F > 3\sigma(F)$ were included in the refinement and using the statistical weight $w = \sigma^{-2}[F_o(\mathbf{H})]$. The multipole expansion was truncated at the hexadecapole ($l_{\text{max}} = 4$) for all non-H atoms and bond-directed dipoles were applied to all H-atoms. A quadrupolar term was added

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