NONLINEAR OPTICAL (NLO) MATERIALS: BIS(2-METHYL-4-NITROANILINIUM) HEXACHLORO-TIN(IV) MONOHYDRATE. QUANTUM CHEMICAL CALCULATIONS. SYNTHESIS, CRYSTAL STRUCTURE, HIRSHFELD SURFACE ANALYSIS.

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Abstract. 2-Methyl-4-nitroaniline (2m4na) and Tin(IV) chloride form a nonlinear optical material, $(2m4na)_2SnCl_6 \cdot H_2O$ (bis(2-methyl-4-nitroanilinium) hexachlorostannate(IV) monohydrate). Crystal structures show alternating cations and anions, forming chain and ring hydrogen-bonding patterns via weak N−H•••Cl bonds. Single-crystal X-ray diffraction determined the structure, with FTIR and UV-visible spectroscopy analyzing composition and electronic transitions. Nonlinear optical properties were studied using Hirshfeld surface analysis and crystal void studies.

Keywords: 2-Methyl-4-nitroaniline; Single crystal; Hydrogen bond; Hirshfeld surface analysis.

Annatatsiya: 2-Metil-4-nitroanilin (2m4na) va qalay (IV) xlorid nochiziqli optik material, (2m4na) $2SnCl_6 \cdot H_2O$ (bis (2-metil-4-nitroanilin) geksaxlorostannat (IV) monogidrat) hosil qiladi. Kristall strukturalarda kationlar va anionlar ketma-ket almashinib, kuchsiz N−H•••Cl bog‘lari orqali zanjir va halqali vodorod bog‘lanish shakllarini hosil qiladi. Bir kristalli rentgen difraksiyasi tuzilishni aniqladi, IQ- va UB-ko‘rinadigan spektroskopiya tarkib va elektron o‘tishlarni tahlil qildi. Nochiziqli optik xususiyatlar Xirshfeld sirt tahlili va kristall bo‘shliqlarni o‘rganish yordamida o‘rganildi.

Kalit so‘zlar: 2-metil-4-nitroanilin; monokristallar; vodorod bog‘lanish; Xirshfeld sirt tahlili.

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Аннотация: 2-Метил-4-нитроанилин (2m4na) и хлорид олова (IV) образуют нелинейный оптический материал (2m4na) $2SnCl_6 \cdot H_2O$ (бис (2-метил-4-нитроанилин) гексахлорстаннат (IV) моногидрат). Кристаллические структуры показывают чередующиеся катионы и анионы, образующие цепные и кольцевые водородные связи посредством слабых связей N−H•••Cl. Монокристаллическая рентгеновская дифракция определила структуру, причем состав и электронные переходы были проанализированы с помощью FTIR и УФ-видимой спектроскопии. Нелинейные оптические свойства были изучены с использованием анализа поверхности Хиршфельда и исследования кристаллической пустоты.

Ключевые слова: 2-Метил-4-нитроанилин; Монокристалл; Водородная связь; Анализ поверхности Хиршфельда.

Introduction.

New organic-inorganic hybrid compounds are vital for blending organic and inorganic properties [1-4]. Their solid-state self-assembly is driven by hydrogen bonding, π-π interactions [5-7], and van der Waals forces [8], shaping supramolecular organization and properties [9-11]. Hydrogen bonds ensure stability, π-π stacking affects electronic and structural features, and van der Waals forces enhance cohesion and packing efficiency[12-15].

Results and discussion. 1.Single crystal X-ray structure analysis.

The intermolecular hydrogen bonds and hydrogen bonds in the molecule are between the N1-H atom in 2-methyl 4-nitro aniline and the Cl2 and Cl3 atoms in $SnCl_4$. The intermolecular bond is N1-H•••Cl3 and N1-H•••Cl2 occurs between Cl2 and between N1-H•••H-O hydrogen bonds. The intermolecular bond is N1-H•••Cl2 distance is 2.579 Å and distance of N1-H•••Cl2 is 2.883 Å. The valence angle of Cl-Sn-Cl in the $SnCl_6^{2+}$ molecule is 92.50 Å.

Information of plane spacing for monoclinic structure crystal systems.

$$\frac{1}{d^2} = \frac{1}{sin^2\beta} \cdot \left(\frac{h^2}{a^2} + \frac{k^2\, sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Additionally, corrections for Lorentz and polarization effects were made to ensure the accuracy of the intensity measurements of the reflections.Monoclinic , Axial lengths and angles -Three unequal axes, one pair not at right angles $a \neq b \neq c$, $\alpha \neq \gamma = 90 \neq \beta$.

The X-ray diffraction data for the crystal structure of 2-Methyl-4-nitrobenzenaminium hexachloro-stannane monohydrate was collected using a KUMA Diffraction KM-4 four-circle single-crystal diffractometer.(Fig-1).

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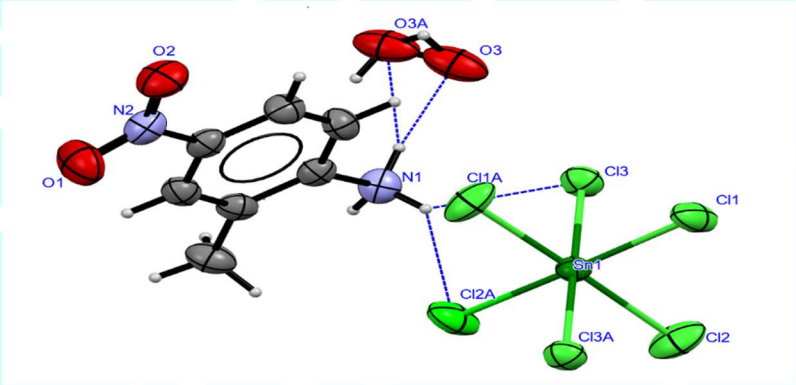


Fig-1. (a) ORTEP drawing of the intermolecular H-bonds and (b) Nonlinear optical (NLO) materials. bis(2-Methyl-4-nitroanilinium) hexachloro-Tin(IV) monohydrate molecule. Thermal ellipsoids are drawn with the 50% probability level.

The diffractometer, equipped with a CCD detector, used graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Raw diffraction data were processed with CrysAlis Data Reduction Program, including absorption correction. Crystal structures of 2-methyl-4-nitroanilinium chloride (1) and bis(2-amino-4-nitroanilinium) hexachloridostannate(IV) monohydrate (2) were solved by direct methods and refined via full-matrix least-squares using SHELXL-97. Crystallographic data: CCDC-875783 (1), CCDC-905995 (2). Supplementary data available free from www.ccdc.cam.ac.uk/conts/retrieving.html or Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). e-mail: deposit@ccdc.cam.uk. Crystallographic data and details of the structure refinement are given in Table-1.

Table-1.

Crystallographic data and details of the refinement of the bis(2-Methyl-4-nitroanilinium) hexachloro-tin(IV) monohydrate. structure.

Name	***bis(2-Methyl-4-nitroanilinium) hexachloro-tin(IV) monohydrate.***
Empirical formula	$2(C_7H_9N_2O_2^+)Cl_6Sn^{2+}\ H_2O$
Formula weight	***655.71***
Temperature/K	***295(2)***
Crystal system	***Monoclinic***
Space group	***C2/c***
a/Å	***12.5392(3)***
b/Å	***9.2956(2)***
c/Å	***20.6018(4)***
α/°	***90***
β/°	***99.435(2)***
γ/°	***90***
V/Å³	***2368.85***
Z	***1***

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ρ_{calc}, g/cm^3	1.342
μ/mm^{-1}	0.895
F(000)	848.0
Crystal size/mm^3	0.16 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
R-Factor(%)	2.06

The transitioning to the compound bis(2-Methyl-4-nitroanilinium) hexachloro-Tin(IV) monohydrate, this complex compound consists of the cation bis(2-Methyl-4-nitroanilinium) and the anion hexachloro-Tin(IV) along with a water molecule forming a monohydrate.

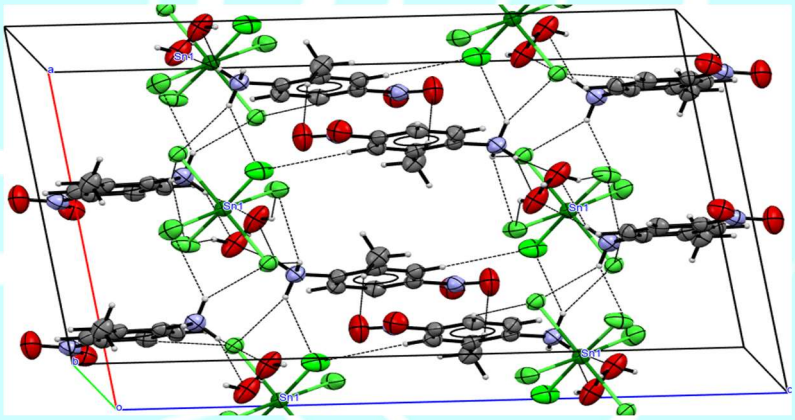


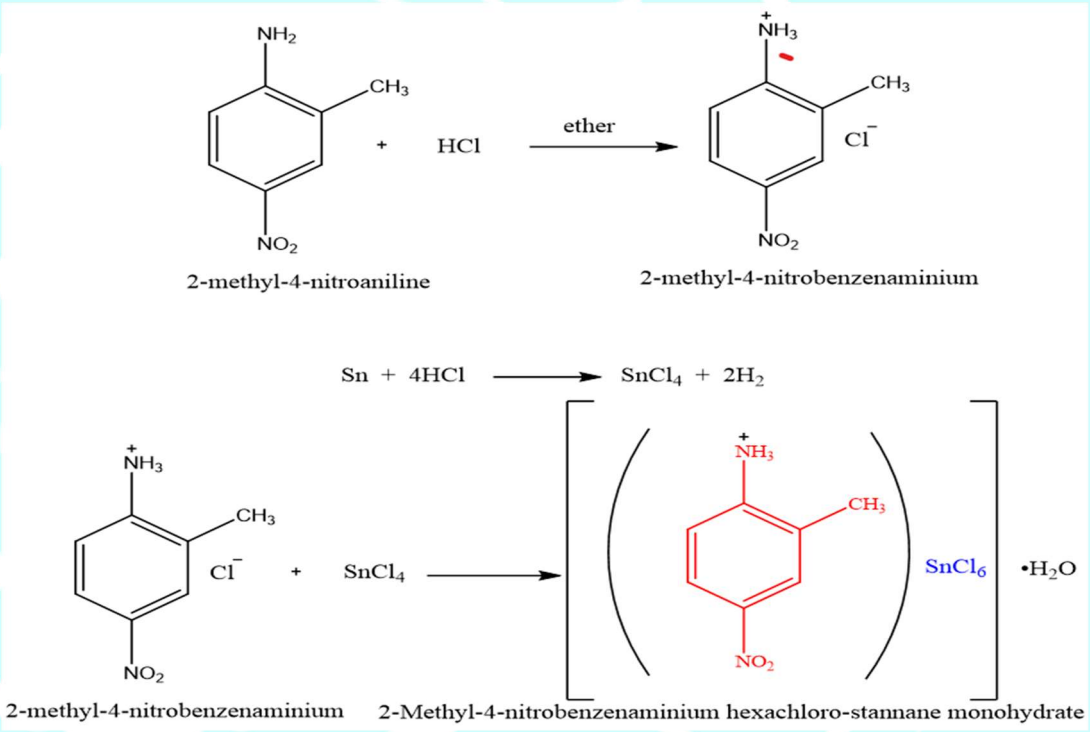
Fig-2. Packing of molecules in the structure of nonlinear optical (NLO) materials. bis(2-Methyl-4-nitroanilinium) hexachloro-Tin(IV) monohydrate

In the crystal structure of bis(2-Methyl-4-nitroanilinium) hexachloro-Tin(IV) monohydrate, the packing of molecules will be influenced by the interactions between the cation, anion, and the water molecule. The coordination number of Tin(IV) in this compound is typically 6, indicating that Tin(IV) is surrounded by six chloride ions (Fig-2).In the crystal structure of 2-Methyl-4-Nitroanilinium Hexachloridostannate(IV), the layers are arranged in an ACC sequence due to the bivalent $SnCl_6^{2-}$ anion balancing two monovalent 2m4na$^+$ ions.

2. Experimental. *Synthesis of bis(2-Methyl-4-nitroanilinium) hexachloro-Tin(IV) monohydrate.*

Synthesis: The initial compounds, 2-Methyl-4-nitroaniline All reagents and solvents used in the synthesis were of reagent grade and employed without additional purification.

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(Scheme-1). Synthesis of bis(2-Methyl-4-nitroanilinium) hexachloro-Tin(IV) monohydrate.

Yellow powder 2-Methyl-4-nitroaniline [Aldrich, purum > 98% (NT)], (0.152g 10 mM) and hydrochloric acid (Aldrich, 35 % in H_2O, 99.95%), (2 mL) were mixed in diethyl ether (10 mL) at room temperature to form a 2-Methyl-4-nitroanilinium chloride precursor solution. The solution was heated to 60 ^{0}C and kept at this temperature for 10 min. Upon cooling, 2-Methyl-4-nitroanilinium chloride precipitated in the solution. The precipitate was then washed with diethyl ether and dissolved in ethanol. Tin shots, weighing 0.118 g (5 mM), were dissolved in 5 mL of 37 % hydrochloric acid at room temperature over seven hours to produce form **tin chloride** ($SnCl_4$). The tin chloride solution was added to the freshly prepared ethanolic solution of the 2-Methyl-4-nitroanilinium chloride precursor while continuously stirring (Scheme-1).

The solution was placed in a thermostat at 25°C for 20-22 days, resulting in the formation of a new crystal.

3. Analysis of Hirshfeld surfaces of discrete nonlinear optical (NLO) materials.

The Hirshfeld surface technique quantitatively analyzes molecular crystalline structures by mapping shifts on the surface due to neighboring atoms, both external and internal. Surfaces are created by partitioning crystal space using the Hirshfeld ratio, where the procrystal is defined by a promolecule with an electron density of 0.5. The normalized contact distance, referred to as d_{norm}, is calculated by considering perspectives from both the exterior and interior of the surface, as outlined below:

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$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}}$$

The parameter denoted as d_{norm} represents the normalized contact distance, where d_e signifies the distance from the Hirshfeld surface to the nearest external nucleus, d_i denotes the corresponding distance to the nearest internal nucleus, and r^{vdW} designates the van der Waals radius of the atom in question.Hirshfeld surface analysis was performed on a (NLO) compound using its CIF file.

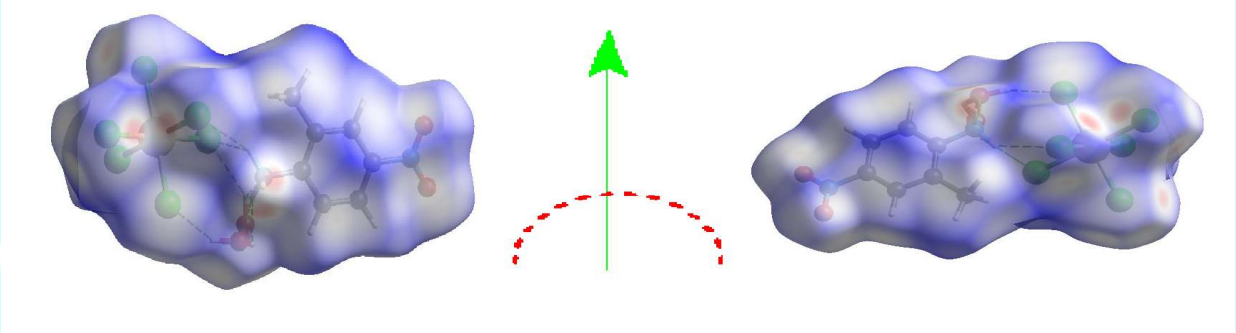


Fig-3. Hirschfeld surface of dnorma nonlinear optical (NLO) materials, interactions inside and outside the surface.

The asymmetric part of the structure was selected for the surface analysis.During the analysis, the Hirshfeld surface was obtained from the normalized contact distance and its d_i and d_e indicators.Quantitative analysis of the Hirschfeld surface area (d_{norm}) revealed that the total volume is 292.86 Å³ and the surface area is 294.76 Å². Generally, larger volume and surface area indicate more extensive intermolecular bonding and interactions within the crystal structure (Fig-3).

The 2D fingerprints of the Hirshfeld surface for the coordination polymer (Fig-5) reveal seven homo- and heteroatomic contact interactions driving crystal packing. Dominant H-O/O-H contacts (55.1%) highlight hydrogen bonding's key role in stabilizing the structure. H---H contacts (11.9%) also significantly contribute to intermolecular packing. Other notable interactions include C---C (1.5%), reflecting van der Waals and dipole-dipole forces, and smaller contributions from All---H/H---All (56.9%), O---H/H---O (8.5%), Cl---O/O---Cl (2.6%), C---H/H---C (2%), and N---O/O---N (0.5%) contacts. Hydrogen contributes 51.3% (inner) and 55.2% (outer), oxygen 36.3% (inner) and 32.5% (outer), while carbon and tin each contribute 0.5% and 0.8% to both inner and outer surfaces, showing similar elemental contributions across the molecula.

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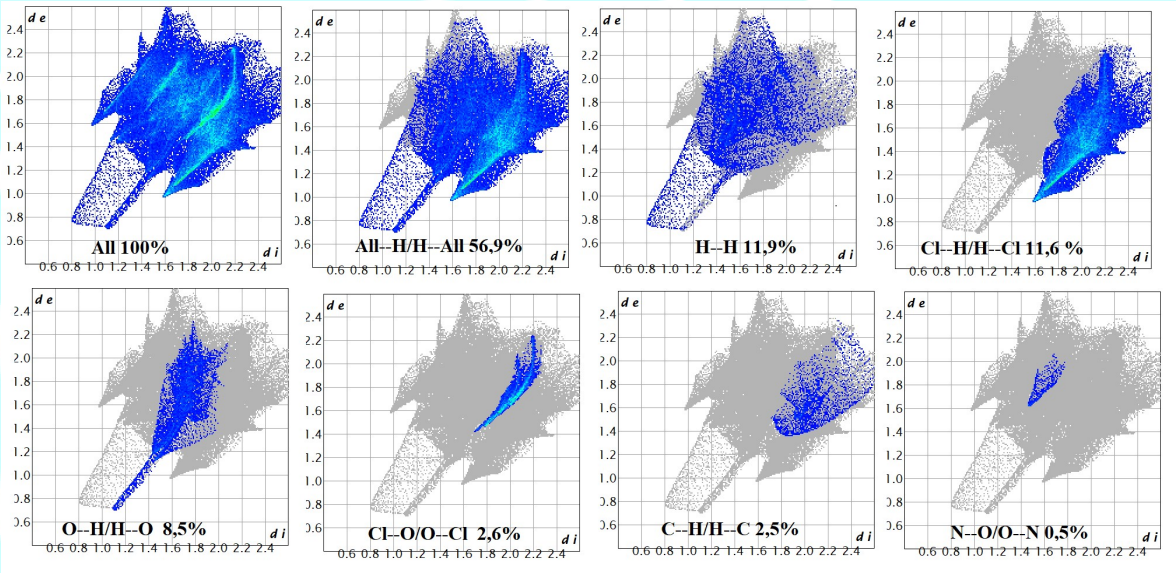


Fig-4. Fingerprint representation of a nonlinear optical (NLO) materials Hirschfeld surface, contribution of interatomic interactions to surface formation.

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