DESIGN, STRUCTURAL ELUCIDATION, DIELECTRIC CHARACTERIZATION, AND HIRSHFELD SURFACE ANALYSIS OF PYRIDIN-2-YLMETHANAMINIUM IODIDE-18-CROWN-6 SUPRAMOLECULAR COCRYSTALS.

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Abstract. Single crystals of pyridin-2-ylmethanaminium iodide-18-crown-6 (PAI18C6) were successfully synthesized via slow evaporation solution growth. Structural elucidation through single-crystal X-ray diffraction revealed that the compound crystallizes in a triclinic system with a centrosymmetric Pī space group. The average C-C and C-O bond lengths within the 18-crown-6 moiety were determined to be 1.4893 Å and 1.4153 Å, respectively. FT-IR spectroscopy confirmed key functional groups, while UV-DRS analysis indicated a direct optical band gap of 3.03 eV, showcasing the material's potential for optoelectronic applications. Thermal analysis demonstrated stability up to 204°C, with a major decomposition event between 204-410°C resulting in 75.8% weight loss. Surface morphology characterized by SEM revealed faceted crystallites and spherical aggregates, with EDS confirming the elemental composition of C, N, O, and I. Dielectric measurements revealed a strong frequency and temperature dependence: the dielectric constant was higher at lower frequencies and increased with temperature, indicating significant interfacial polarization effects. Hirshfeld surface and fingerprint plot analyses highlighted that H•••H (66.4%), I•••H/H•••I (18.2%), and O•••H/H•••O (7.4%) interactions dominate the intermolecular landscape.

Keywords: Crystal structure • dielectric studies • Optical studies •Hirshfeld surface

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Annotatsiya: Piridin-2-ilmetanaminiy yodid-18-kraun-6 (PAI18C6) monokristallari sekin bug‘latuvchi eritmani o‘stirish yo‘li bilan muvaffaqiyatli sintez qilindi. Monokristall rentgen nurlari difraksiyasi yordamida strukturaviy yoritish shuni ko‘rsatdiki, birikma markazga simmetrik Pī fazoviy guruhi bilan triklinik tizimda kristallanadi. 18-kraun-6 qismidagi C-C va C-O bog‘larining o‘rtacha uzunligi mos ravishda 1,4893 Å va 1,4153 Å ekanligi aniqlandi. FT-IQ spektroskopiyasi asosiy funksional guruhlarni tasdiqladi, UB-DRS tahlili esa 3,03 eV to‘g‘ridan-to‘g‘ri optik taqiqlangan zona kengligini ko‘rsatdi, bu esa materialning optoelektron qo‘llanilish imkoniyatlarini namoyish etdi. Termik tahlil 204°C gacha barqarorlikni ko‘rsatdi, 204-410°C oralig‘ida asosiy parchalanish hodisasi natijasida 75,8% vazn yo‘qotildi. SEM bilan tavsiflangan sirt morfologiyasi qirrali kristallitlar va sferik agregatlarni aniqladi, EDS C, N, O va I element tarkibini tasdiqladi. Dielektrik o‘lchashlar chastota va haroratga kuchli bog‘liqlikni ko‘rsatdi: past chastotalarda dielektrik doimiysi yuqori va harorat oshishi bilan oshadi, bu sezilarli fazalararo qutblanish ta’sirini ko‘rsatadi. Xirshfeld yuzasi va barmoq izi diagrammasi tahlillari shuni ko‘rsatdiki, H•••H (66,4%), I•••H/H•••I (18,2%) va O•••H/H•••O (7,4%) o‘zaro ta’sirlar molekulalararo landshaftda ustunlik qiladi.

Kalit so‘zlar: Kristall tuzilmalar, dielektrik xususiyatlar tadqiqoti, optik xususiyatlar o‘rganish, Hirshfeld sirt tahlili.

Аннотация:Были успешно синтезированы монокристаллы пиридин-2-илметанаминия иодида-18-краун-6 (PAI18C6) методом медленного испарения раствора. Структурное прояснение монокристаллической рентгеноструктурной дифракцией показало, что соединение кристаллизуется в триклинной системе с центросимметричной пространственной группой Pī. Средние длины связей C-C и C-O в пределах фрагмента 18-кроны-6 составили соответственно 1,4893 Å и 1,4153 Å. FT-ИК-спектроскопия подтвердила наличие ключевых функциональных групп, в то время как анализ УФ-ДРС показал прямой оптический полосовой зазор 3,03 эВ, что демонстрирует потенциал материала для оптоэлектронных применений. Термический анализ показал стабильность до 204°C, причем основное событие разложения между 204-410°C привело к потере веса на 75,8%. Морфология поверхности, характеризующаяся СЭМ, выявила фасеточные кристаллиты и сферические агрегаты, причем ЭДС подтверждает элементный состав C, N, O и I. Диэлектрические измерения выявили сильную зависимость от частоты и температуры: диэлектрическая проницаемость была выше на более низких частотах и увеличивалась с температурой, что указывало на значительный эффект поляризации

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между фазами. Анализ поверхностных и отпечатковых графиков Хиршфельда показал, что H•••H (66,4%), I•••H/H•••I (18,2%) и O•••H/H•••O (7,4%) взаимодействия доминируют в межмолекулярном ландшафте.

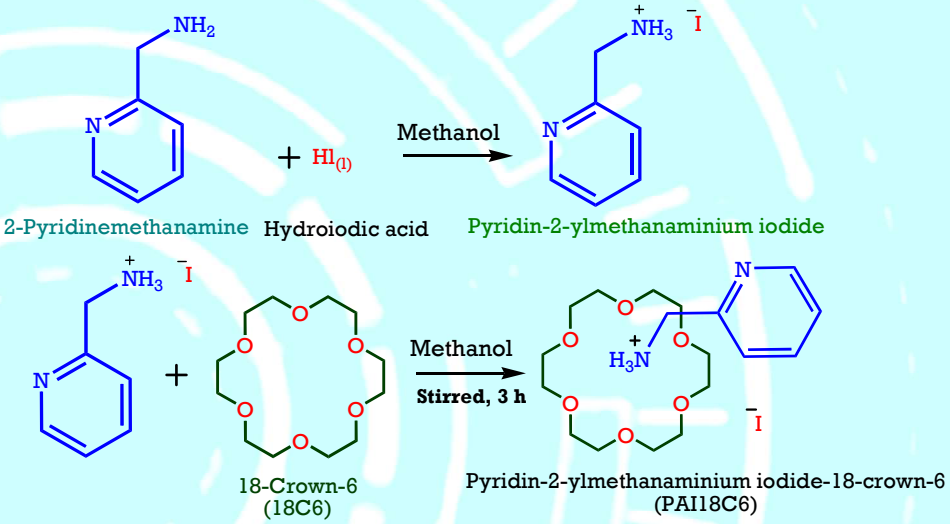
Ключевые слова: кристаллическая структура, диэлектрические исследования, оптические исследования, поверхность Хиршфельда.

Introduction.

Crown ethers, first discovered by Charles Pedersen in 1967, are cyclic compounds with carbon chains surrounding a central ring of five or six oxygen atoms[1-3]. These molecules, with oxygen as electron-rich donors and carbon as bridges, are key in supramolecular and coordination chemistry. Notably, 18-crown-6 (18C6) excels at encapsulating guest ions or molecules, driving its use in materials science and crystal engineering[5-7]. Their macrocyclic structure enables stable host-guest complexes, formed via noncovalent interactions like hydrogen bonding, π–π stacking[8], and hydrophobic effects, leading to well-defined supramolecular architectures[9]. These complexes are versatile, with applications in ion separation, sensing, nonlinear optics, and phase-transfer catalysis. While 18C6's structural versatility is well-known, its interactions with guests like pyridin-2-ylmethanaminium were underexplored[10-12]. Our study introduces novel cocrystals, analyzing their structural, optical, and dielectric properties, inspired by data-driven modeling and machine learning advancements in functional materials[12-15].

2.Synthesis of pyridin-2-ylmethanaminium iodide-18-crown-6 (PAI18C6). The synthesis process began by mixing equimolar amounts of 2-pyridinemethanamine (pyridin-2-ylmethanamine) and hydroiodic acid (57% aqueous solution) in 20 mL of methanol at room temperature. The reaction mixture was stirred for 30 minutes to ensure the complete formation of the pyridin-2-ylmethanaminium iodide precursor. Separately, 18-crown-6 (18C6) was completely dissolved in 30 mL of methanol under ambient conditions

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Scheme 1. Synthesis of PAI18C6.

After dissolution, the freshly prepared methanolic solution of pyridin-2-ylmethanaminium iodide was slowly added dropwise to the 18C6 solution under continuous stirring. The combined solution was stirred for an additional 3 h at room temperature to promote homogeneity and interaction between the components (Scheme 1). The resulting clear solution was then left undisturbed at room temperature to undergo slow evaporation. After approximately 16 to 18 d, well-formed single crystals suitable for X-ray diffraction analysis were obtained. The crystals were carefully collected by filtration, washed with a small amount of cold methanol to remove any residual impurities, and air-dried at room temperature.

Single-crystal XRD analysis. The single-crystal X-ray diffraction study provided detailed insights into the structure of PAI18C6. The compound crystallizes in the triclinic crystal system with a centrosymmetric *P*$\bar{1}$ space group. The molecular structure was refined with displacement ellipsoids drawn at the 35% probability level, as depicted in Fig. 1. The crystallographic data and parameters are provided in Table 1, with bond parameters listed in Table-1, and atomic coordinates and displacement parameters detailed in Tables-2,3. Crystal systems and space groups of various 18-crown-6-based host-guest complexes are summarized in Table 2. It was observed that most of these complexes crystallized in centrosymmetric monoclinic systems , with common space groups such as $P2_1/c$, $P2_1/n$, and $C2/m$. A few complexes, including [(4-cyano-1-methylpyridinium)$_2$-(18C6)] diiodide, bis(1,3-dimethylpyridin-1-ium iodide)-18C6, bis(1,4-dimethylpyridin-1-ium iodide)-18C6, and the present pyridin-2-ylmethanaminium iodide-18C6, crystallized in the triclinic system with the centrosymmetric P$\bar{1}$ space group. Establishing general reasons for the observed crystal symmetries remains difficult. It is quite likely that specific molecular orientations, host-guest interactions, and crystal packing effects play a decisive role in determining the final symmetry.

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The asymmetric unit comprises one pyridin-2-ylmethanaminium cation, one iodide anion, and a single 18C6 molecule. A robust network of non-covalent interactions plays a crucial role in stabilizing the crystal lattice. Among these, extensive N─H•••O hydrogen bonds dominate the structure, where the protonated amino group of the pyridin-2-ylmethanaminium cation engages in bifurcated hydrogen bonding with oxygen atoms of the 18C6 ring. The average N─H•••O hydrogen bond distance is 2.9347 Å, reflecting a strong and directional interaction that significantly enhances the rigidity and stability of the supramolecular assembly. In addition to these dominant interactions, C─H•••I hydrogen bonds between the organic cation/18C6 complex and the iodide anions further reinforce the three-dimensional framework. These contacts contribute to the overall cohesion of the lattice by linking adjacent molecular units. The spatial arrangement and geometric parameters of the hydrogen bonds are illustrated in Fig. 1(a), with detailed bond lengths and angles summarized in Table 3. Furthermore, π•••π stacking interactions between adjacent pyridine rings were observed, which further stabilize the crystal structure. The centroid-to-centroid distance between aromatic rings is measured at 3.803 Å, and the stacking angle is approximately 20.22°, consistent with typical values for effective π•••π interactions (~3.8 Å). The stacking follows a slipped parallel arrangement, with horizontal displacements between aromatic rings ranging from 1.357 to 1.371 Å and a mean interplanar distance of 3.645 Å, as shown in Fig. 1(b).Within the 18-crown-6 ring, the oxygen atoms are arranged alternately above and below the macrocyclic plane, maintaining the flexible and accommodating conformation characteristic of crown ethers. The bond length analysis reveals that the average C–C and C–O bond distances within the 18C6 molecule are 1.4893 Å and 1.4153 Å, respectively. These values slightly deviate from those reported for uncomplexed 18C6 (C–C: 1.507 Å; C–O: 1.411 Å), suggesting slight structural distortions upon complex formation, most likely due to host–guest interactions and hydrogen bonding constraints.

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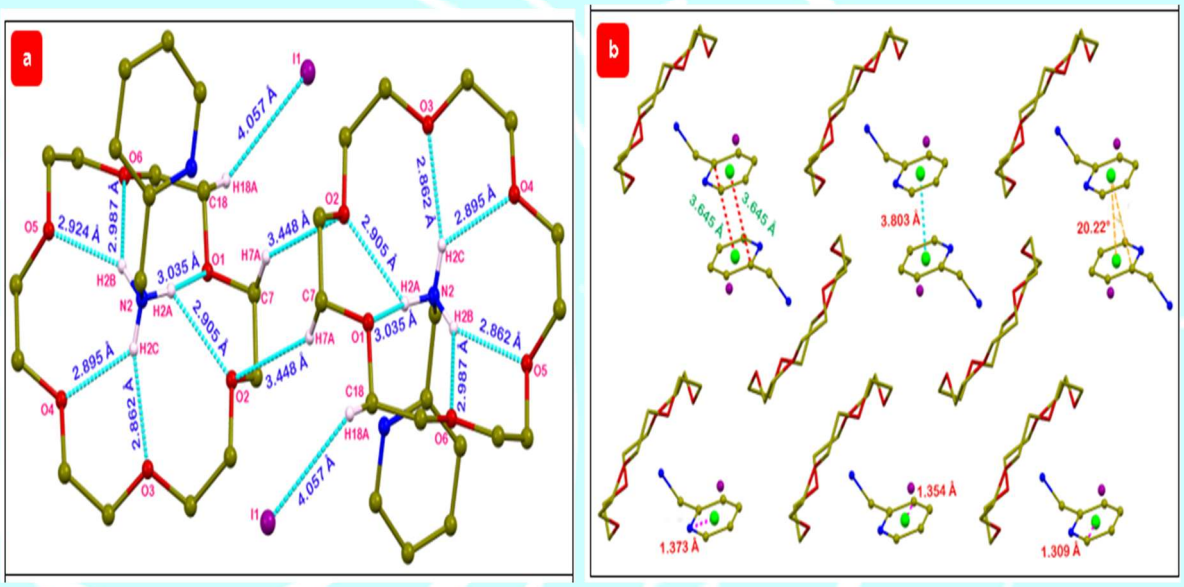


Fig. 1 (a) Hydrogen bonding network in PAI18C6, displaying significant N–H•••O and C–H•••I interactions that contribute to crystal stabilization and (b) π•••π stacking interactions between aromatic rings, highlighting additional non-covalent stabilization within the crystal lattice.

Table-1.

Crystal data and structure refinement for PAI18C6.

CCDC	*2344788*
Chemical formula	$C_{18}H_{33}IN_2O_6$
Formula weight (g/mol)	*500.36*
Temperature (K)	*298(2)*
Wavelength (Å)	*0.71073*
Crystal size (mm)	*0.210 x 0.270 x 0.290*
Crystal system	*Triclinic*
Space group	*Pī*
a, b, c (Å)	*9.068(9), 10.843(13), 11.679(12)*
α, β, γ (°)	*96.06(6), 92.40(5), 101.09(6)*
Volume (Å^3)	*1118.(2)*
Z	*2*
Independent reflections	*6578 [R(int) = 0.1028]*
Coverage of independent reflections	*96.30%*
Goodness-of-fit on F^2	*1.006*

Table 2.

Crystal systems and space groups of some 18-crown-6-based host-guest complexes.

Host guest complexes	Crystal System	Space group
Bis(1-Methylpyridinium iodide)-18C6	*Monoclinic*	C2/*m*

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Bis(2-Amino-1-methylpyridin-1-ium iodide)-18C6	*Monoclinic*	$P2_1/n$
Bis(3-Amino-1-methylpyridin-1-ium iodide)-18C6	*Monoclinic*	$P2_1/n$
Bis(4-Amino-1- methylpyridin-1-ium iodide)-18C6	*Monoclinic*	$C2/m$
Bis(4-Amino-1-ethylpyridin-1-ium iodide)-18C6	*Monoclinic*	$C2/m$
Bis(1,2-Dimethylpyridin-1-ium iodide)-18C6	*Monoclinic*	$P2_1/n$
Bis(1,3-Dimethylpyridin-1-ium iodide)-18C6	*Triclinic*	$P\bar{1}$
Bis(1,4-Dimethylpyridin-1-ium iodide)-18C6	*Triclinic*	$P\bar{1}$
Bis(1,3-Dimethylimidazol-3-ium iodide)-18C6	*Monoclinic*	$P2_1/n$
Bis(1H-Benzimidazol-3-ium iodide)-18C6	*Monoclinic*	$P2_1/n$
Bis(3-Hydroxy-1-methylpyridin-1-ium iodide)-18C6	*Monoclinic*	$P2_1/c$
[(4-Cyano-1-methylpyridinium)2-(18C6)] diiodide	*Triclinic*	$P\bar{1}$
18C6-2-Methoxyethanaminium periodate	*Monoclinic*	$P2_1/c$
Pyridin-2-ylmethanaminium iodide-18C6	*Triclinic*	$P\bar{1}$

Table 3.

Hydrogen bonds for PAI18C6 [Å and].

D-H•••A	d(D-H)	d(H•••A)	d(D•••A)	<(DHA)
N(2)-H(2B)•••O(5)	0.89	2.163	2.924(4)	143.2
N(2)-H(2B)•••O(6)	0.89	2.266	2.987(4)	137.9
N(2)-H(2C)•••O(3)	0.89	2.068	2.862(4)	148.0
N(2)-H(2C)•••O(4)	0.89	2.253	2.895(4)	128.9
N(2)-H(2A)•••O(1)	0.89	2.318	3.035(4)	137.6
N(2)-H(2A)•••O(2)	0.89	2.283	2.905(4)	126.9
C(7)-H(7A)•••O(2)	0.97	2.630	3.448(5)	142.2
C(1)-H(1)•••I(1)	0.93	3.244	3.953(5)	134.6
C(18)-H(18A)•••I(1)	0.97	3.191	4.057(5)	149.6

REFERENCES.

1. Y. Zhao, K. Zhu, Organic–inorganic hybrid lead halide perovskites for optoelectronic and electronic applications, Chem. Soc. Rev. 45(3) (2016) 655-689, https://doi.org/10.1039/C4CS00458B.

2. M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites, Science, 338(6107) (2012) 643-647, https://doi.org/10.1126/science.1228604.

ISSN 3030-3907

3. T. Chen, Z. Deng, W. Lu, M. Lu, J. Xu, F. Mao, C. Li, C. Zhang, K. Wang, Pillar-Supported 2D Layered MOFs with Abundant Active-Site Distributions for High-Performance Alkaline Supercapacitors, Inorg. Chem. 63(40), (2024) pp.18699-18709. https://doi.org/10.1021/acs.inorgchem.4c02479.
4. H. Yuping, G. Galli, Perovskites for Solar Thermoelectric Applications: A First Principle Study of CH3NH3AI3 (A = Pb and Sn), Chem. Mater. 26 (2014) 5394–5400, https://doi.org/10.1021/cm5026766.
5. F. Hao, C.C. Stoumpos, R.P. Chang, M.G. Kanatzidis, Anomalous band gap behavior in mixed Sn and Pb perovskites enables broadening of absorption spectrum in solar cells, J. Am. Chem. Soc. 136(22) (2014) 8094-8099, https://doi.org/10.1021/ja5033259.
6. L. Dimesso, M. Dimamay, M. Hamburger, W. Jaegermann, Properties of CH3NH3PbX3 (X = I, Br, Cl) Powders as Precursors for Organic/Inorganic Solar Cells, Chem. Mater. 26 (2014) 6762–6770, https://doi.org/10.1021/cm503240k.
7. T.C. Wei, S. Mokkapati, T.Y. Li, C.H. Lin, G.R. Lin, C. Jagadish, J.H. He, Nonlinear absorption applications of CH3NH3PbBr3 perovskite crystals, Adv. Funct. Mater. 28(18) (2018) 1707175, https://doi.org/10.1002/adfm.201707175.
8. D. Lencer, M. Salinga, M. Wuttig, Design rules for phase-change materials in data storage applications, Adv. Mater. 23(18) (2011) 2030-2058, https://doi.org/10.1002/adma.201004255.
9. L. Lanzetta, J.M. Marin-Beloqui, I. Sanchez-Molina, D. Ding, S.A. Haque, Two-dimensional organic tin halide perovskites with tunable visible emission and their use in light-emitting devices, ACS Energy Lett. 2(7) (2017) 1662-1668, https://doi.org/10.1021/acsenergylett.7b00414.
10. W.Q. Liao, Y. Zhang, C.L. Hu, J.G. Mao, H.Y. Ye, P.F. Li, S.D. Huang, R.G. Xiong, A lead-halide perovskite molecular ferroelectric semiconductor, Nat. Commun. 6 (1) (2015) 1–7, https://doi.org/10.1038/ncomms8338.
11. J.G. Bednorz, K.A. Müller, Perovskite-type oxides-the new approach to high-Tc superconductivity, Rev. Mod. Phys. 60(3) (1988) 585, https://doi.org/10.1103/RevModPhys.60.585.
12. J.G. Bednorz, K.A. Müller, Perovskite-Type Oxides-the New Approach to High-Tc Superconductivity, Nobel Lecture, Angew. Chem., Int. Ed. Engl. 27(5) (1988) 735-748, https://doi.org/10.1103/RevModPhys.60.585.
13. Y. Takahashi, R. Obara, Z.Z. Lin, Y. Takahashi, T. Naito, T. Inabe, S. Ishibashi, K. Terakura, Charge-transport in tin-iodide perovskite CH3NH3 SnI3: origin of high conductivity, Dalton Trans. 40(20) (2011) 5563-5568, https://doi.org/10.1039/c0dt01601b.

ISSN 3030-3907

14. B. Chen, S. Wang, Y. Song, C. Li, F. Hao, A critical review on the moisture stability of halide perovskite films and solar cells, Chem. Eng. J. 430 (2022) 132701, https://doi.org/10.1016/j.cej.2021.132701.
15. K. Ramalingam, T. Rajaraman, Metal-organic hybrids of tin (IV) with tuneable band gap: Synthesis, spectral, single crystal X-ray structural, BVS and CSM analysis of morpholinium hexahalostannate (IV), J. Mol. Struct. 1218 (2020) 128489, https://doi.org/10.1016/j.molstruc.2020.128489.

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