OVERVIEW OF 18-CROWN-6 BASED SUPRAMOLECULAR STRUCTURES FOR NONLINEAR OPTICAL (NLO) PROPERTIES

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Abstract. 18-Crown-6 (18C6) and pyridine-3-ylmethanamine (1:2 ratio) form self-assembled supramolecular cocrystals. Single-crystal X-ray analysis revealed a monoclinic, centrosymmetric Pn space group structure, driven by N-H•••O and O-H•••O interactions. FT-IR and micro-Raman confirmed functional groups, while diffuse reflectance showed a *2.84eV* bandgap. Hirshfeld surface and fingerprint plots highlighted robust crystal packing interactions. Third-order nonlinear optical properties were assessed via Z-scan technique.

Keywords.pyridin-3ylmethanamine;1,4,7,10,13,16hexaoxacyclooctadecane; 1,4,7,10,13,16-hexaoxacyclooctadecane, pyridin-3-ylmethanaminium salt; hydrogen bond; crystal data; FT-IR spectroscopy.

Annatatsiya: 18-Kraun-6 (18C6) va piridin-3-ilmetanamin (1:2 nisbatda) o‘z-o‘zidan yig‘ilgan supramolekulyar kokristallarni hosil qiladi. Monokristall rentgen tahlili N-H•••O va O-H•••O o‘zaro ta’sirlar bilan boshqariladigan monoklinik, markazga simmetrik Pn fazoviy guruh tuzilishini aniqladi. FT-IQ va mikro-Raman funksional guruhlarni tasdiqladi, diffuz qaytarish esa 2,84eV taqiqlangan zonani ko‘rsatdi. Xirshfeld yuzasi va barmoq izlari grafiklari mustahkam kristall to‘plamlarning o‘zaro ta’sirini ta’kidladi. Uchinchi tartibli nochiziqli optik xususiyatlar Z-skanerlash usuli yordamida baholandi.

Kalit so‘zlar: piridin-3-ilmetanamin;1,4,7,10,13,16geksaoksatsiklooktadekan; 1,4,7,10,13,16-geksaoksatsiklooktadekan, piridin-3-ilmetanaminiy tuzi; vodorod bog‘i; kristall ma’lumotlari; FT-IQ-spektroskopiya.

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Аннотация: 18-Кроун-6 (18C6) и пиридин-3-илметанин (1:2) образуют самосборные надмолекулярные кокристаллы. Монокристаллический рентгеноструктурный анализ выявил моноклинную, центросимметричную пространственную групповую структуру Pn, обусловленную взаимодействиями N-H•••O и O-H•••O. FT-IR и микро-Raman подтвердили функциональные группы, в то время как диффузное отражение показало полосу пропускания 2,84eV. Графики поверхности Хиршфельда и отпечатков пальцев выявили прочные взаимодействия кристаллической упаковки. Нелинейные оптические свойства третьего порядка оценивались методом Z-сканирования.

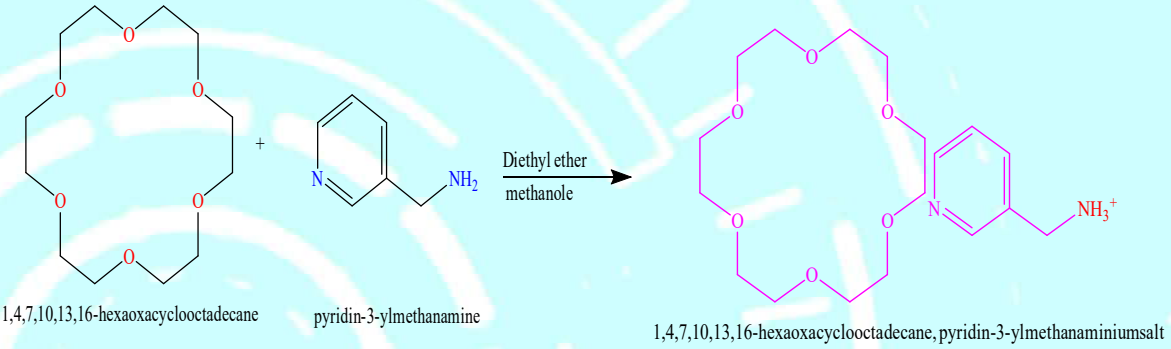
Ключевые слова: пиридин-3илметанамин; 1,4,7,10,13,16 гексаоксациклооктадекан;1,4,7,10,13,16-гексаоксациклооктадекан, пиридин-3-илметанаминовая соль; водородная связь; кристаллические данные; ИК-спектроскопия.

Introduction.

Crown ethers are pivotal in supramolecular and coordination chemistry due to their ability to form host-guest complexes with unique structures and diverse bonding interactions[1-3].Supramolecular networks arise from weak intermolecular interactions, including hydrogen bonds, charge transfer, and van der Waals forces[8]. These materials find applications in data storage, capacitors, sensors, and optical devices [9-11]. Third-order nonlinear optical properties of the crystal ere examined by the Z-scan technique. Hirshfeld surface analysis was used to quantify intra- and intermolecular interactions[12-13].

Experimental.Synthesis and crystal growth.18-Crown-6 (18C6) and pyridin-3-ylmethanamine (P3MA) were procured from Sigma Aldrich (Assay:99%), while commercially available solvents from Merck were used without further purification. In a solvent system consisting of diethyl ether (5 mL) and methanol (10 mL) in a 1:2 (v/v) ratio, 18C6 (1.32 g, 5mmol) and pyridin-3-ylmethanamine (P3MA) (1.08 g, 10 mmol) were combined in a stoichiometric ratio of 1:2. The resulting mixture underwent reflux at 95-100 °C for 4 h (Scheme 1). Maintained in a constant temperature thermostat at 40 °C, crystallization occurred over 25–27 days, yielding crystals with dimensions of 1 × 2 × 1 mm³ (Yield: 80%). (Scheme-1).

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(Scheme-1). Synthesis of 18-Crown-6, pyridin-3-ylmethanaminium salt.

Single crystal X-ray structure analysis.The crystal structure was elucidated by single-crystal XRD analysis. Crystallographic data and details of the refinement parameters are listed in Table-1.

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

The selected hydrogen bonds, bond distances and bond angles are listed in Tables 2-4. The ORTEP and packing diagram of 18C6•2(P3MA)•2(H2O) are given in Fig-1. It crystallizes in the monoclinic system with centric space group Pn with Z = 2. This caused bad data quality and high wR2 value.Most of the amine/ammonium (R-NH2, R-NH3+, etc.) containing crown ether complexes form N─H•••O/N-H•••O type of hydrogen bonds [15–17]. In the present study, the hydrogen bonds are only.OW─H•••O18C6 because of the inclusion of water molecules in the crown ether cavity.

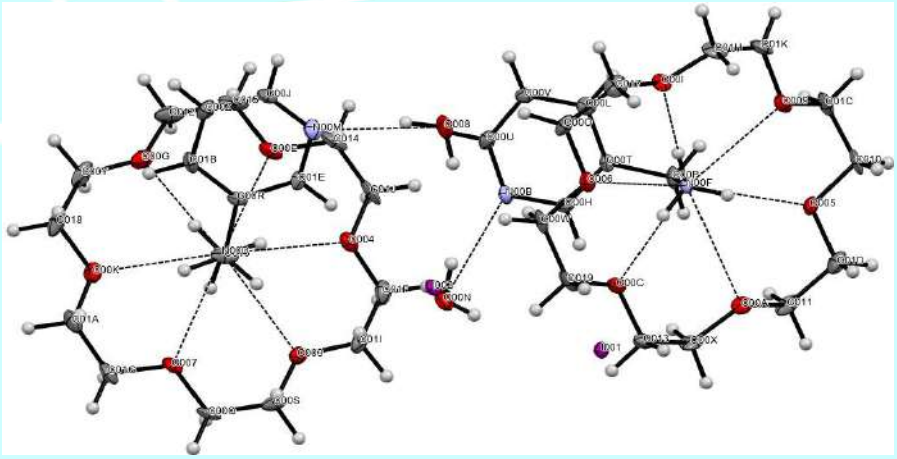


Fig-1. (a) ORTEP drawing of the intermolecular H-bonds and (b) Nonlinear optical (NLO) materials. 1,4,7,10,13,16-hexaoxacyclooctadecane, pyridin-3-ylmethanaminium salt.molecule. Thermal ellipsoids are drawn with the 50% probability level.

Table -1.

Crystal data and structure refinement for [(P3MA)2+·2(18C6)]·2H₂O.

Identification code	exp_393_CB08_auto
Empirical formula	$C_{36}H_{68}I_2N_4O_{14}$

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Formula weight ;Temperature/K	1034.74;107(5)
Crystal system; Space group	Monoclinic;Pn
a/Å, b/Å, c/Å	12.7(10), 9.45(10), 19.25(10)
α/° β/° γ/°	90;92.3510(10); 90
Volume/Å^3 ,Z; ρ_{calc}g/cm^3; μ/mm^{-1}	2311.56(3) ,2;1.487; 11.216
F(000); Crystal size/mm^3	1060; 0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.594 to 143.192
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -23 ≤ l ≤ 23
Reflections collected	45306

Table-2.

Hydrogen bonds for [(P3MA)2+·2(18C6)]·2H₂O. (A0); R = 0.03.

D-H•••A	d(D-H)	d(H•••A)	<DHA	d(D•••A)	Symmetry
O(008) – H(00Y) •••N(00M)	0.8700	2.0200	2.866(6)	164.00	
N(00D) – H(00S) ••• O(003)	0.9100	2.5100	2.994(5)	114.00	
N(00D) – H(00S)••• O(007)	0.9100	2.0000	2.817(5)	149.00	
N(00D) – H(00S)••• O(00K)	0.9100	2.6000	2.918(5)	101.00	
N(00D) – H(00T) •••O(004)	0.9100	1.9900	2.876(6)	165.00	
N(00F) – H(00L)••• O(009)	0.9100	2.5500	2.898(5)	103.00	
N(00F)–H(00L)•••O(00I)	0.9100	2.0000	2.906(5)	177.00	
N(00F)– H(00M)•••O(00A)	0.9100	2.5800	3.012(5)	109.00	
O(00N)– H(G) •••N(00B)	0.87(8)	2.11(8)	2.914(6)	154(8)	**1/2+x,1-y,1/2+z**

Table-3.

Bond Distances [(P3MA)2+·2(18C6)]·2H₂O (A^0). R = 0.03

Bond	Distances	Bond	Distances
O(007) –C(00Q)	1.416(7)	O(00N)–H(G)	0.87(8)
O(007) –C(01G)	1.440(7)	O(00N)–H(00)	0.77(8)
O(00E)–C(014)	1.428(7)	N(00D)–C(016)	1.499(6)
O(00E)–C(015)	1.412(8)	N(00M) –C(01E)	1.340(7)

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O(00G) –C(00Y)	1.429(7)	N(00M)–C(00J)	1.331(8)
O(005)–C(01D)	1.435(7)	C(00Q) –C(00S)	1.489(8)
O(005)–C(010)	1.438(7)	C(00Y)–C(018)	1.507(8)
O(006)–C(00W)	1.424(7)	C(012)–C(015)	1.501(8)
O(006)–C(00O)	1.403(7)	C(014)–C(01J)	1.489(9)
C(01J) –H(01R)	0.9900	C(01K)–H(3)	0.9500
C(010)–C(01C)	1.497(9)	C(00P)–C(00T)	1.503(7)

Table-4.

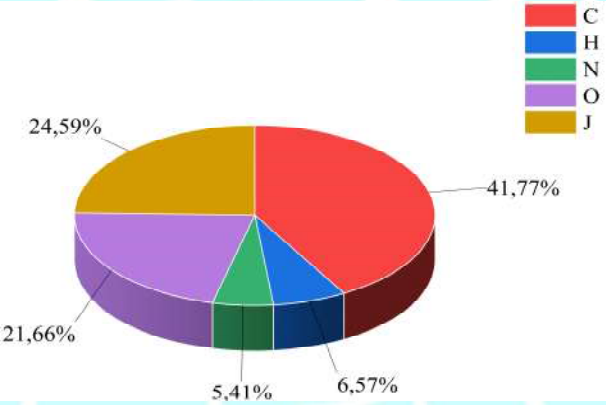
Bond Angles. (A^0). R = 0.03

Bond	Bond Angles	Bond	Bond Angles
C(00P) –N(00F)–H(00L)	109.00	H(00A) –C(00Q) –H(00B)	108.00
C(00P)–N(00F)–H(00M)	109.00	H(00C) –C(00S) –H(00D)	108.00
C(00Y)–C(018)–H(01G)	110.00	O(00A) –C(00X) –C(013)	108.9(5)
H(01I)–C(01A)–H(01J)	108.00	O(005) –C(010) –C(01C)	109.3(5)
O(00C)–C(013)–H(01X)	110.00	O(009) –C(01K) –H(3)	126.00
H(01W)–C(013)–H(01X)	108.00	N(00B) –C(00H) –C(00T)	123.5(4)
O(00I)–C(017)–H(B)	110.00	C(00T) –C(00L) –C(00V)	118.5(5)
N(00F)–C(00P)–C(00T)	112.9(4)	C(016)–C(00R) –C(01B)	121.3(5)
C(00H)–C(00T)–C(00P)	120.6(4)	C(016) –C(00R) –C(01E)	120.3(4)
C(00L)–C(00T)–C(00P)	121.1(4)	C(01B) –C(00R) –C(01E)	118.4(5)
C(00H) –C(00T) –C(00L)	118.2(4)	C(00J) –C(00Z) –C(01B)	118.2(5)
N(00B)–C(00U)–C(00V)	123.5(5)	N(00D) –C(016) –C(00R)	112.5(4)
C(00L)–C(00V)–C(00U)	119.3(5)	C(00R) –C(01B) –C(00Z)	118.9(5)

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N(00B) –C(00H) – H(00N)	118.00	N(00M) –C(01E)– C(00R)	122.9(5)
C(00T) –C(00H) – H(00N)	118.00	C(00Z) –C(00J) – H(00X)	118.00

The percent elemental composition of compound 1,4,7,10,13,16-hexaoxacyclooctadecane, pyridin-3-ylmethanaminium salt was determined using a Thermo Scientific FlashSmart (CHNS/O) elemental analyzer. This analysis was performed by gas chromatographic separation of combustion gases based on the modified Dumas method.In order to assess the accuracy of the measurements, the results obtained from the analysis were compared in practical and theoretical terms.Table-5.



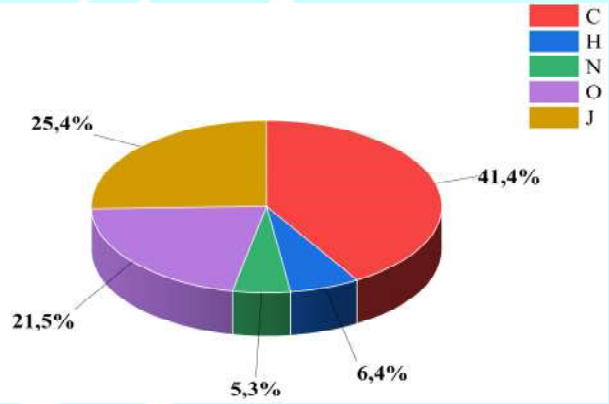


Table-5.

Compound	*Mr*	*Compared*	*C %*	*H %*	*N %*	*O %*
$C_{36}H_{68}I_2N_4O_{14}$	*1034.12 gr/mole*	*Theoretical*	*41.77*	*6.57*	*5.41*	*21.66*
		Practical	*41.39*	*6.42*	*5.29*	*21.46*

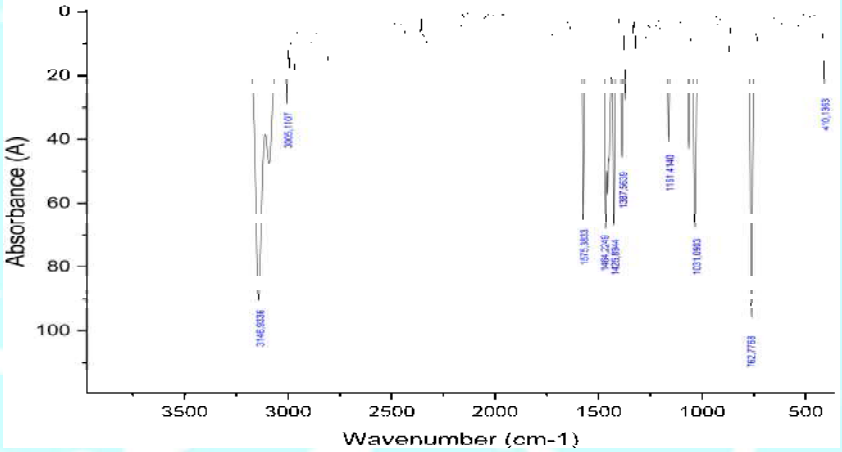
Table-6.

FT-IR spectroscopy. The characteristics vibrational spectra of (I)-(V) are shown in Table-6. Below is a detailed analysis of the peaks you provided.

Peak (cm^{-1})	Assigment	Functional group
3147	N-H stretching	$-CH_2-NH_3^+$ (protonated methanaminium group)
3005	Aromatic C-H stretching	Pyridine ring
1575	Aromatic C=C stretching or N-H bending	Pyridine ring or $-CH_2-NH_3^+$
1464	Aromatic C-C stretching or N-H bending	Pyridine ring or $-CH_2-NH_3^+$
1425	Aromatic ring deformation or C-H bending	Pyridine ring
1387	Symmetric C-H bending	$-CH_2-$ group

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1161	Ether C-O stretching	Crown ether (-C-O-C-)
1031	Ether C-O stretching	Crown ether (-C-O-C-)
762	Out-of-plane C-H bending	Pyridine ring
410	Metal-ligand interaction or ring deformation	Crown ether or pyridine ring



FT-IR spectroscopy-1,4,7,10,13,16-hexaoxacyclooctadecane, pyridin-3-ylmethanaminium salt.

Z-scan studies. The nonlinear absorption, nonlinear refractive index, and third-order nonlinear susceptibility were determined by standard equations . The NLO properties of the cocrystal were experimentally determined by the Z-scan technique. Here, the open and closed aperture Z-scan curves are used for nonlinear absorption and nonlinear refractive index measurements. The transmittance intensity variations corresponding to the z values, and the closed and open aperture z-scan curves are represented

Hirshfeld surface analysis. Description of the Hirshfeld surface analysis is quite detailed and informative. Hirshfeld ratio, where the procrystal is effectively delineated by employing a promolecule characterized by an electron density of 0.5. The Hirshfeld surface is defined as the region in space where the ratio of the molecule's electron density (P_{mol}) to the total electron density $\rho_{total} = \rho_{mol} + \rho_{env}$ equals 0.5**.**

The normalized contact distance, referred to as $\boldsymbol{d_{norm}}$, is as outlined below:

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

Quantitative analysis of the Hirshfeld surface revealed that the total volume was 599.64 Å^3 and the surface area was 470.26 Å^2. The crystal structure was analyzed using Hirshfeld surface analysis. The normalized contact distance d_{norm} ranged from -0.1281 to 1.4477 a.u. The 2D fingerprints of the Hirshfeld surface are shown in Fig-1. The most prominent intermolecular interactions were H•••H contacts, which accounted for 57.8% of the Hirshfeld surface.

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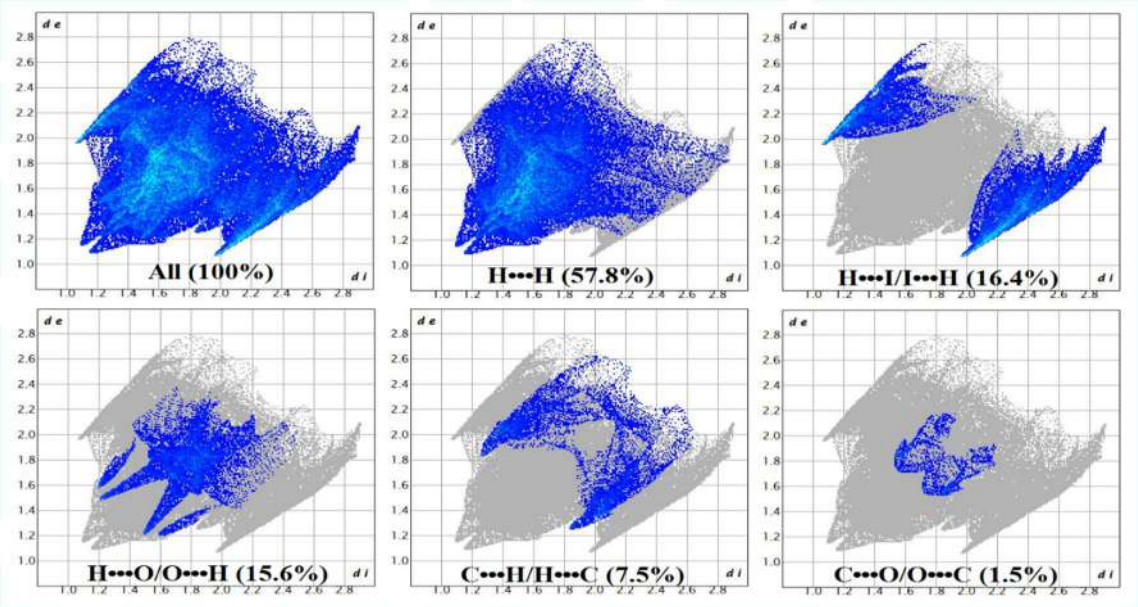


Fig-1.Hirschfeld surface fingerprint representation, contribution of interactions to surface formation.

The second largest contributor was H•••I/I•••H contacts, making up 16.4% of the surface. Other notable contributions include H•••O/O•••H contacts (15.6%), C•••H/H•••C contacts (7.5%), and C•••O/O•••C contacts (1.5%). These reflect the various van der Waals and dipole-dipole interactions present in the crystal.Hirshfeld surface, demonstrating the diversity of intermolecular interactions stabilizing the crystal structure of compound **(NLO).**

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