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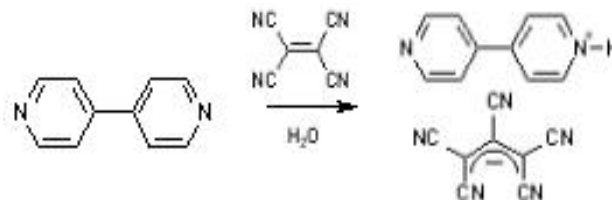
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4,4'-BIPYRIDINIUM 1,1,2,3,3-PENTACYANOPROPENIDE — NEW CONVENIENT BUILDING BLOCK FOR THE CRYSTAL ENGINEERING

The successful combination of the known tectones — 4,4'-bipyridinium cation and 1,1,2,3,3-pentacyanopropenide anion — demonstrate a promising for study and modifications crystal structure with four strong intermolecular interactions of different types and directions (three orthogonal), namely: resonance-stabilized H-bonds, aromatic π -stacking, π -stacking of acyclic systems, and Coulomb attraction amplified by multiple C—H...N contacts; furthermore, there are four groups of chemically equivalent H-bonds directed along the same axis and two different anion geometries in seemingly equal environments. Crystal data: $a=9.767(4)$, $b=13.465(8)$, $c=14.274(7)$ Å, $\alpha=97.67(4)^\circ$, $\beta=107.89(3)^\circ$, $\gamma=108.19(4)^\circ$, $V=1642(2)$ Å³, space group $P\bar{1}$ (N 2).

It is not recently that chemists cowork with physicists on creation and investigation of new materials with properties requisite for technical progress, and it is a traditional part of chemist to find a substance promising to have derivatives with required qualities. In this respect 4,4'-bipyridines and its derivatives are very useful because of their unique physical properties [1, 2]. The 4,4'-bipyridine mono-salts, related to well-known and used widely viologens [1], are convenient tectones for the crystal engineering of functional materials. Nevertheless there are only a few communications on the synthesis and structural investigation of the such systems [3—5].

In this paper we report the crystal structure investigation of 4,4'-bipyridinium 1,1,2,3,3-pentacyanopropenide. The 4,4'-bipyridinium 1,1,2,3,3-pentacyanopropenide was synthesized by hydrolysis [6] (scheme below) of 4,4'-bipyridine · tetracyanoethylene complex [7] in refluxing aqueous ethanol (96 %). The substance may also be obtained by simple metathetical reaction [6] from commercially available 4,4'-bipyridine and readily synthesizable pentacyanopropenide salts [8]:



A suitable crystal was selected from the mother liquid and mounted to a glass fibre. Data were collected on Enraf-Nonius CAD4 diffractometer (graphite monochromated irradiation). Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on azimuthal scan data [9] was applied. The structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using CRYSTALS program package [10]. Crystallographic data are presented in table, molecular structure, the numbering scheme and selected geometrical parameters are given in fig. 1.

The crystal lattice consists of alternating layers of cations and anions, with Coulomb attraction being amplified by multiple C—H...N short contacts

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Crystallographic data for 4,4'-bipyridinium 1,1,2,3,3-pentacyanopropenide

Formula	C ₁₈ H ₉ N ₇	Volume	1642(2) Å ³	Refinement on	F ²
CCDC deposit no	287006	Z	4	Reflections used	2571
Formula weight	646.63 g·mol ⁻¹	Calculated density	1.308 g·cm ⁻³	I/σ(I) cutoff	2
Temperature	288 K	Absorption coefficient	0.691 cm ⁻¹	Parameters	499
Crystal class	triclinic	Radiation	CuK _α , β-filtered	Goodness of fit	0.9102
Space group	P T (N 2)	θ range	3.363–60.041°	Chebyshev weighting	10.9, 13.6, 5.57
a	9.767(4) Å	Index ranges	–10 ≤ h ≤ 10,	scheme coefficients	
b	13.465(8) Å		–15 ≤ k ≤ 14,	R(F)	0.072
c	14.274(7) Å		0 ≤ l ≤ 16,	wR(F ²)	0.107
α	97.67(4)°	Reflections measured	5203	Δρ _{min}	Δρ _{max}
β	107.89(3)°	Unique reflections	4869		
γ	108.19(4)°	Crystal size, mm	0.06×0.09×0.25		

(fig. 2, figures have 1 unit cell depth, unit cell is shown). Cationic layers are formed by aromatic π-stacking of antiparallel linear threads of H-bonded cations (fig. 3).

Three named interactions are orthogonal and the fourth, π-stacking of acyclic anions, is directed at about 45° to interactions in cationic layers and is orthogonal to Coulomb attraction (fig. 3). This forms a rich base for studies of directional properties, such as compressibility, electric and magnetic susceptibility, etc.

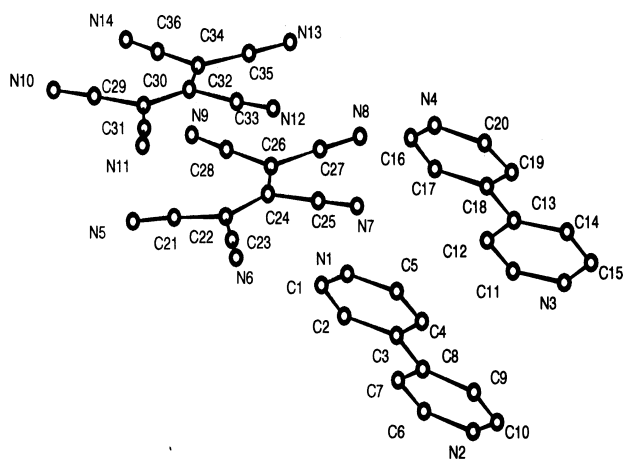


Fig. 1. Perspective view and numbering scheme of 4,4'-bipyridinium 1,1,2,3,3-pentacyanopropenide. Selected bond lengths (Å) and angles (°): C(3)–C(8) 1.494(8), C(13)–C(18) 1.478(8), N(1)–C(1) 1.318(8), N(1)–C(5) 1.341(8), N(2)–C(6) 1.331(8), N(2)–C(10) 1.346(8), N(3)–C(11) 1.336(8), N(3)–C(15) 1.335(8), N(4)–C(16) 1.332(8), N(4)–C(20) 1.344(9); C(1)–N(1)–C(5) 120.9(5), C(6)–N(2)–C(10) 118.0(5), C(11)–N(3)–C(15) 120.8(5), C(16)–N(4)–C(20) 117.3(5).

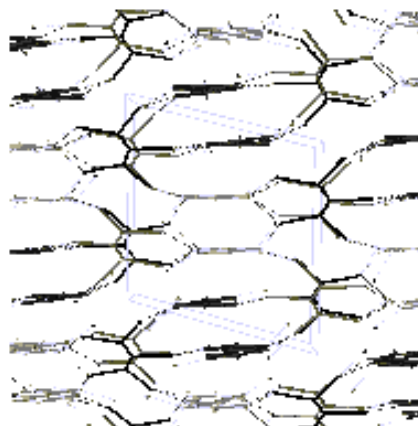


Fig. 2. View along H-bonds. Short C–H...N contacts are shown (dotted), expanded — in black, hanging — in light grey. Coulomb attraction is directed horizontally, aromatic π-stacking of cations — vertically, π-stacking of acyclic anions — from top above the figure plane to below under the figure plane.

Anions are found to have two geometries, planar and spirally distorted, without any explicit difference of the environment. This provokes a question about the geometry of anions and lattice symmetry under pressure and is subject to ab initio calculations.

Both cations [11] and anions [12] are fluorescent. Together with their unusual arrangement, network of C–H...N contacts capable of excitation transfer between layers and π-stacking for exchange between neighboring anions (and cations) with different geometry, the case is very reach for optical studies, especially for those employing polarized irradiation.

Considering the resonance-stabilized [13] nature

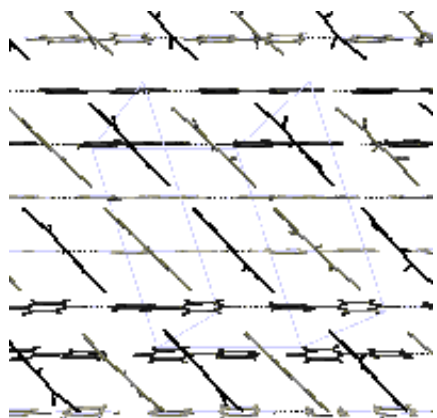


Fig. 3. View normal to layers. H-bonds (dotted) are directed horizontally, aromatic π -stacking of cations — vertically, π -stacking of acyclic anions — from lower left to upper right corner, Coulomb attraction between layers is perpendicular to figure plane. Planar anions are given in grey, distorted — in black.

of H-bonds (invariability of molecular structure to proton transfer), their strength ($d(\text{N}\cdots\text{N}) = 2.73 \text{ \AA}$), parallel directivity and the absence of other movable particles in the structure we suggest that the synchronous intermolecular proton transfer with the loss of inversion centers is possible under application of electric field, moving force being the arousal of strong dipole moment compensating the outer electric field. The effect should show up as an abrupt change in inductivity and the field dependence of hydrogen position should be observable by neutronography or precision X-ray studies.

Finally, both cations and anions are well-known [6] and simple, allowing variety of modifications to be done to achieve such goals of crystal engineering as selective exclusion/inclusion of desired interaction in an already complex system or creation of noncentrosymmetric structure to develop non-linear optics.

РЕЗЮМЕ. Удачная комбинация двух известных тектонов — катиона 4,4'-бипиридиния и аниона 1,1,2,3,3-пентацианопропиленида — демонстрирует многообещающую для исследований и модификаций кристаллическую структуру с четырьмя сильными межмолекулярными взаимодействиями различных типов и направленности (три из которых взаимно ортогональны), а именно: резонансно-стабилизированные водородные связи, ароматический π -стекинг, π -стекинг ациклических систем и кулоновское притяжение, усиленное C—H \cdots N-

контактами. Более того, в кристалле четыре группы химически эквивалентных водородных связей направлены вдоль одной оси; два аниона имеют разные геометрические параметры в приблизительно одинаковом окружении. Основные кристаллографические параметры: $a=9.767(4)$, $b=13.465(8)$, $c=14.274(7) \text{ \AA}$, $\alpha=97.67(4)$, $\beta=107.89(3)^\circ$, $\gamma=108.19(4)^\circ$, $V=1642(2) \text{ \AA}^3$, пространственная группа $P \bar{1} (N 2)$.

РЕЗЮМЕ. Вдале поєднання двох відомих тектонів — катиону 4,4'-біпіридинію та аніону 1,1,2,3,3-пентаціанпропіленіду — демонструє багатообіцяючу для досліджень та модифікацій кристалічну структуру з чотирма сильними міжмолекулярними взаємодіями різних типів та направленості (три з яких ортогональні), а саме: резонансно-стабілізовані водневі зв'язки, ароматичний π -стекинг, π -стекинг ациклических систем та кулонівське притягання, посилене C—H \cdots N-контактами. Більше того, у кристалічному стані чотири групи хімічно еквівалентних водневих зв'язків направлені вздовж однієї осі; два аніони мають різні геометричні параметри у приблизно однаковому оточенні. Основні кристаллографічні параметри: $a=9.767(4)$, $b=13.465(8)$, $c=14.274(7) \text{ \AA}$, $\alpha=97.67(4)$, $\beta=107.89(3)^\circ$, $\gamma=108.19(4)^\circ$, $V=1642(2) \text{ \AA}^3$, просторова група $P \bar{1} (N 2)$.

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