

MOLECULAR AND SUPRAMOLECULAR STRUCTURE OF 4,4'-BIPYRIDINIUM DIODIDE

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Abstract:

The structure of 4,4'-bipyridinium diiodide has been determined. The diprotonated cation possesses crystallographic inversion symmetry with the pyridyl rings coplanar. The crystal packing is dominated by weak but directional N-H...I (N...I distance of 3.47(2) Å) and C-H...I (C...I distances of 3.74(3)3.77(3) Å) interactions to give layers of ions. The layers stack parallel to the (101) direction and are linked together by an additional C-H...I interaction (C...I distance of 3.816(5) Å). Crystal data: triclinic, *P*-1 (No. 2), *a* = 8.2940(13), *b* = 8.3842(11), *c* = 5.0978(8) Å, α = 93.761(11)°, β = 112.281(12)°, γ = 106.887(11)°, *V* = 307.63(8) Å³, *Z* = 1, *S*_{calc} = 2.22 g/cm³. Final residual values based on 997 observed (*I* > 2σ(*I*)) reflections: *R* = 0.026, *R*_w = 0.034.

Article:

INTRODUCTION

Increasing interest in inorganic/organic composite materials is related to their potential for possessing a wide variety of properties associated with either of the individual components. For example, inorganic polymers have been combined with organic spacers to produce crystals with interesting nonlinear optical properties, and which can serve as "crystal host-guest lattices" [1]. Metal complexes with organic ligands capable of polymerizing either *in situ* [2] or in the solid state [3] have led to three-dimensional network structures consisting of polymeric inorganic arrays which are organically cross-linked. Pyrazine and bipyridine spacers have been combined with metal cyanide complexes to generate novel supramolecular structures [4].

Organic components have also been exploited as structure-directing templates for the isolation of metastable composites which retain the structural elements of the synthetic precursors [5]. Recent examples utilizing the diprotonated 4,4'-bipyridinium cation include the stabilization of molybdenum oxide layers ([Mo₇O₂₂]²⁻) [6] and the isolation of a new anionic lead iodide chain structure [7]. Although this cation has been reported with a wide variety of counterions, no structural details are available for any of the simple dihalide salts. The structure of the dibromide salt has been reported [8], but structural details were not given and are not available through the Cambridge data base. This report provides the first such information for the diiodide salt, and describes an interesting variety of N-H...I and C-H...I interactions that dominate the crystal packing.

EXPERIMENTAL

Synthesis. Dark red crystals of the title compound, 4,4'-bipyridinium diiodide, C₁₀H₁₀N₂I₂ (1), were obtained as a side product during the synthesis of viologen bisphosphonate diiodide, {(HO)₂P(O)CH₂CH₂-(bipyridinium)-CH₂CH₂(O)P(OH)₂}I₂.

Following the previously reported synthesis of viologen bisphosphonate dibromide [9], 1.807 g (10 mmol) of 4,4'-dipyridyl (Aldrich) was added to 100 mL of purified water and the mixture stirred for about 1 h. In another 100 mL of water was dissolved 5.867 g (7.6 mmol) of diethyl(2-bromoethylphosphonate) (Aldrich). The 4,4'-dipyridyl mixture was gradually added to the diethyl solution in a three-neck, round-bottom flask fitted with a stirrer, reflux condenser, and thermometer. Temperature was increased gradually until the solid dissolved. The clear solution was then refluxed for 15 h. Fifteen milliliters of concentrated hydriodic acid (Aldrich) was added

to the hot solution and refluxed for an additional 2 h. Slow evaporation of this solution yielded dark-red tabular crystals.

TABLE 1
Crystallographic Data for **1**

Formula	C ₁₀ H ₁₀ N ₂ I ₂
CCDC deposit no.	CCDC-1290/48
Formula weight (g mol ⁻¹)	412.00
Color	red
Habit	tabular
Dimensions (mm)	0.10 × 0.30 × 0.40
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	8.2940(13)
<i>b</i> (Å)	8.3842(11)
<i>c</i> (Å)	5.0978(8)
α (°)	93.761(11)
β (°)	112.281(12)
γ (°)	106.887(11)
<i>V</i> (Å ³)	307.63(8)
<i>Z</i>	1
<i>D</i> _{calc} (g cm ⁻³)	2.22
μ (cm ⁻¹)	2.29
Transmission factors	0.79-1.00
Reflections collected	1166
Reflections unique (<i>R</i> _{merge})	1084 (0.016)
<i>hkl</i> range	10, ±10, ±6
Reflections observed (<i>I</i> > 2σ(<i>I</i>))	997
<i>R</i> (<i>F</i>) ^a ; <i>R</i> _w (<i>F</i>) ^b	0.026; 0.034
(Δ/σ) _{max}	0.002
ρ _{min} ; ρ _{max}	-0.93; 0.96

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w(F_o)^2} \right]^{1/2}$$

TABLE 2
Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
I (1)	11643 (1)	8268 (1)	284 (1)	46 (1)
N (1)	8054 (6)	7467 (6)	2487 (9)	48 (2)
C (2)	7957 (8)	5859 (7)	2577 (12)	52 (2)
C (3)	6759 (7)	4853 (6)	3603 (12)	46 (2)
C (4)	5672 (6)	5521 (5)	4497 (8)	32 (2)
C (5)	5882 (7)	7241 (6)	4456 (11)	45 (2)
C (6)	7086 (8)	8187 (7)	3438 (12)	52 (2)
H (1)	876 (8)	814 (7)	179 (12)	47 (14)
H (2)	888 (12)	548 (11)	221 (18)	93 (24)
H (3)	661 (9)	372 (9)	368 (14)	63 (17)
H (5)	523 (6)	774 (6)	492 (10)	30 (12)
H (6)	713 (11)	957 (10)	350 (17)	94 (24)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor

X-ray Crystallography. All measurements were made at 22 ± 1°C on a Nicolet R3mV diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data (10, ± 10, ±6) within the range 3.5 < 2θ < 50° were measured using ω/2θ scans. The intensities of three reflections (3 −3 −1; 2 −1 −2; −2 −4 2) monitored periodically throughout data collection indicated no need for a decay correction (±2% fluctuation). The data were corrected for Lorentz and polarization effects, and for absorption using an empirical method based on azimuthal (ψ) scans of several moderately intense reflections (transmission factors: 0.79-1.00).

The structure was solved by direct methods and refined by full-matrix least-squares techniques. The asymmetric unit consists of an iodide anion in a general position and a centrosymmetric cation situated about an inversion center (1/2, 1/2, 1/2) which is coincident with the midpoint of the central C-C bond. All non-hydrogen atoms were refined with anisotropic vibrational parameters; hydrogen atoms were located by standard difference-Fourier methods and were refined with isotropic vibrational parameters. Structure solution, refinement, and the calculation of derived parameters for both compounds were performed with the NRCVAX suite of programs [10] and with SHELXTL-Plus [11]. Neutral atom scattering factors used were those of Cromer and Waber [12], and the real and imaginary anomalous dispersion corrections were those of Cromer [13]. Relevant crystallographic data are given in Table 1. Final positional parameters and equivalent isotropic displacement parameters are reported in Table 2, and distances and angles within the cation and between cations and anions are listed in Table 3.

RESULTS AND DISCUSSION

The structure of **1** consists of discrete 4,4'-bipyridinium cations and iodide anions (see Fig. 1) which form a layer stabilized by weak, but directional N-H...I and C-H...I interactions (Fig. 2). The layers stack along the

crystallographic (1 0 1) direction; adjacent layers are linked by an additional C-H...I interaction (Fig. 3). Distances and angles within the cation agree with those of previously reported examples [14, 15]. Diprotonated 4,4'-bipyridinium cations, like their monoprotonated and neutral derivatives, can exhibit torsional flexibility about the central C-C bond. Previously reported examples of 4,4'-bipyridinium cations can be grouped into two categories: (1) non-planar cations with torsional angles ranging from 17(1) to 38.4(9)° [14], and (2) planar cations with a torsional angle between the pyridyl rings at or nearly 0.0° [15]. The cation in **1** falls into the latter category, as the two pyridyl rings are coplanar, allowing it to possess crystallographic inversion symmetry. There is no evidence, such as difference Fourier peaks or unusual displacement parameters, to indicate that the observed model represents an averaged structure of disordered non-planar cations.

TABLE 3
Selected Bond Distances (Å) and Angles (°) for **1**

Distances			
N(1) – C(2)	1.332 (8)	N(1) – C(6)	1.33 (1)
N(1) – H(1)	0.89 (6)	C(2) – C(3)	1.391 (9)
C(2) – H(2)	0.98 (11)	C(3) – C(4)	1.381 (9)
C(3) – H(3)	0.92 (8)	C(4) – C(5)	1.404 (7)
C(4) – C(4a)	1.481 (9)	C(5) – C(6)	1.372 (9)
C(5) – H(5)	0.86 (6)	C(6) – H(6)	1.15 (9)
H(1)···I(1)	2.75 (4)	C(2)···I(1b)	3.818 (5)
H(2)···I(1b)	3.15 (5)	C(6)···I(1c)	3.740 (5)
H(6)···I(1c)	2.98 (5)	C(6)···I(1d)	3.816 (5)
H(6)···I(1d)	3.18 (5)		
Angles			
C(2) – N(1) – C(6)	122.5 (6)	C(2) – N(1) – H(1)	123 (5)
C(6) – N(1) – H(1)	115 (5)	N(1) – C(2) – C(3)	119.6 (6)
N(1) – C(2) – H(2)	118 (5)	C(3) – C(2) – H(2)	122 (5)
C(2) – C(3) – C(4)	120.0 (5)	C(2) – C(3) – H(3)	124 (5)
C(4) – C(3) – H(3)	116 (5)	C(3) – C(4) – C(5)	118.0 (5)
C(3) – C(4) – C(4a)	121.8 (5)	C(5) – C(4) – C(4a)	120.2 (6)
C(4) – C(5) – C(6)	119.9 (6)	C(4) – C(5) – H(5)	124 (3)
C(6) – C(5) – H(5)	116 (4)	N(1) – C(6) – C(5)	119.9 (5)
N(1) – C(6) – H(6)	126 (5)	C(5) – C(6) – H(6)	114 (5)
N(1) – H(1)···I(1)	139 (3)	C(2) – H(2)···I(1b)	126 (3)
C(6) – H(6)···I(1c)	123 (3)	C(6) – H(6)···I(1d)	116 (3)

Atoms labeled with a lower-case character were generated by the following symmetry operation:

- a) 1 – x, 1 – y, 1 – z
- b) 2 – x, 1 – y, – z
- c) 2 – x, 2 – y, – z
- d) 2 – x, 2 – y, 1 – z

The most interesting aspect of **1** involves the crystal packing. The N···I distance of 3.47(2) Å lies just within the sum of van der Waals radii of 1.55 Å for nitrogen and 1.98 Å for iodine [16], and the C···I distances of 3.74(3)–3.77(3) Å are outside the range for carbon (1.70 Å) and iodine. However, the N···I distance is considerably shorter than the sum of normalized non-bonded contact radii more recently determined by systematic analysis of a large number of intermolecular contact distances (1.75 Å for carbon, 1.61 Å for nitrogen, and 2.00 Å for iodine) [17], and the C···I distances are just at the limit of these values. More importantly, all of these contacts exhibit angular characteristics (see Table 2) resembling those accepted for conventional and weak C-H···X hydrogen bonding [18]. As has been recently pointed out, these types of interactions should not be thought of as van der Waals contacts, but as electrostatic attractions whose viability as a function of distance falls off much more slowly [19].

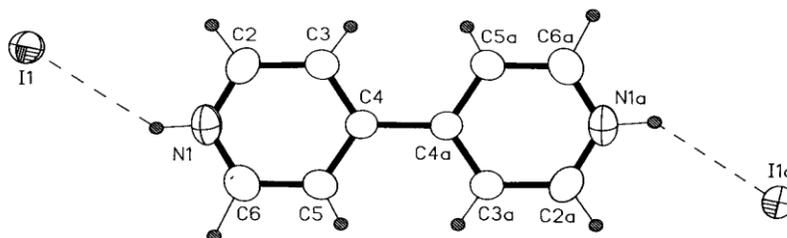


FIG. 1
Thermal ellipsoids at the 50% level and the numbering scheme for **1**.

It has been our experience for polyatomic anions involving iodine, such as polyiodides (I_{x+2n}^{x-}) and cadmium tetraiodide (CdI_4^{2-}), in which negative charge is distributed over several atoms, that salts with cations containing good hydrogen bonding donors often incorporate guest molecules capable of serving as hydrogen bonding acceptors. These acceptors include water [20-22], nonprotonated molecules of the nitrogen heterocycle [21], or others such as methylquinone [21]. Crystallization of **1** as a simple salt from a solution containing a variety of suitable guests is indicative of the strength of this type of interaction, and supports its utility for crystal engineering applications.

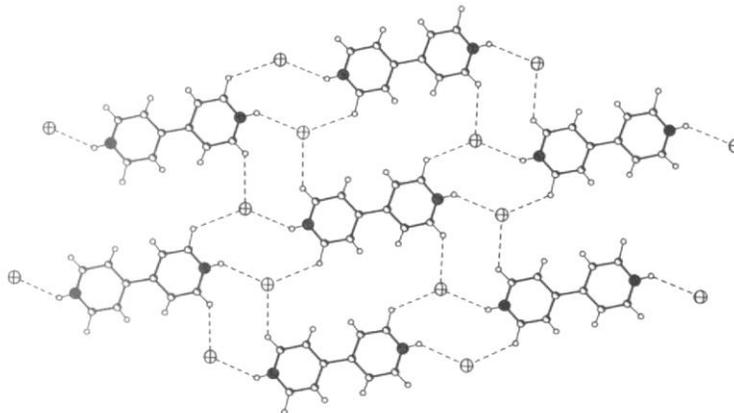


FIG. 2

Layered structure of **1**. N-H...I and C-H...I interactions shown as dashed lines. Iodide anions are shown as thermal ellipsoids, nitrogen atoms as filled circles, carbon atoms as open circles, and hydrogen atoms as smaller open circles.

Close analogs of **1** include the monoclinic [15b] and orthorhombic [14b] polymorphs of 4,4'-bipyridinium dinitrate, and 4,4'-bipyridinium bromotetrabromo dicuprate(II) [15d]. Both nitrate salts possess N-H...O hydrogen bonding (N...O distances: monoclinic, 2.770(5) Å; orthorhombic, 2.670(3) Å); both also possess C-H...O interactions that have reasonable angular characteristics for electrostatic attraction (C...O distances: monoclinic, 3.163(6)3.204(6) Å; orthorhombic, 3.176(4)-3.239(4) Å). Although the local geometry of these interactions bear some similarity to those of **1**, there are no obvious relationships between the packing of the ions in either of these forms and that of **1**. The bromotetrabromodicuprate(II) salt contains N-H...Br (2.57 and 2.45 Å) and C-H...Br (2.80 Å) interactions that influence the crystal packing.

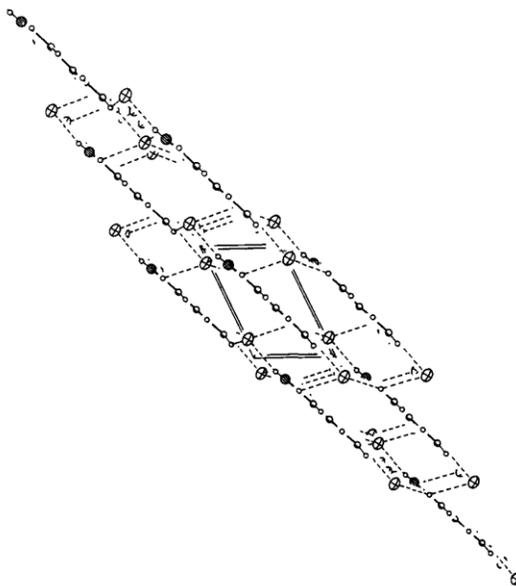
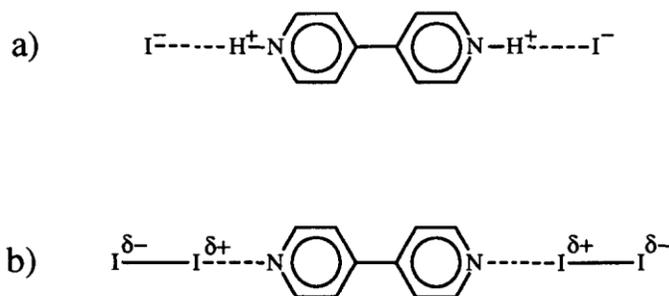


FIG. 3

Packing diagram for **1** viewed down the **b**-axis, parallel to the layers, which are stacked along the (1 0 1) direction. Origin is the lower, left, rear corner; +x is up; +y is out; +z is to the right.

As in 1, the crystal packing in the neutral 4,4'-bipyridine as the dihydrate is also the result of a balance between stronger interactions, in this case N...H-O hydrogen bonding, and weaker C-H...O interactions [23]. The stronger interaction between the nitrogen atom of bipyridine and the water molecule links the components into infinite chains. The weaker interactions stabilize the chains and associate them into layers. The major difference in the two compounds results from the presence of strong water...water hydrogen bonding which orients the layers in such a way that separate stacks of bipyridine molecules and waters of hydration are formed. These interactions also allow for a non-planar conformation of the bipyridine molecules. In 1, there is no strong directional interaction to self-associate the iodides or bipyridyl cations, and weak interlayer C-H...I interactions favor a more staggered stacking of the layers, and consequently a planar conformation for the bipyridine fragment.

The N-H...I interaction in 1 (Scheme 1 a) is related to that of an N...I-I charge transfer interaction (Scheme 1b) [24], but the packing interactions for the two moieties are quite different. The stronger directional nature of the $n \rightarrow \sigma^*$ interaction and the significant differences in packing sterics for this compound preclude the formation of weak C-H...I interactions as observed in 1. More favorable van der Waals contacts involving the uncomplexed end of the I₂ molecule separate the organic and iodine portions of 4,4'-bipyridine•2I₂ into regions. The packing in the charge transfer complex is more akin to that seen in the neutral dihydrate structure described above, and as was seen there the difference in packing requirements is also reflected in a non-planar conformation of the 4,4'-bipyridine molecule (torsion angle is 25.1(7)°).



SCHEME 1

CONCLUSIONS

The supramolecular structure of the first halide salt of the diprotonated 4,4'-bipyridinium cation is dominated by weak interactions involving the large, soft iodide anion. Comparison of this structure with known derivatives (4,4'-bipyridine dihydrate and 4,4'-bipyridine•2I₂) possessing stronger, more directional interactions reveals significant similarities and differences. Completion of the series with the bromo and chloro-derivatives should provide for a continuum of interaction strengths and directionalities which will prove useful for predicting the structures of additional 4,4'-bipyridine complexes and 4,4'-bipyridinium salts.

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