X-ray Structure Analysis Online

Synthesis and Crystal Structure of Bis pyridinium 1,2-Ethane periodate

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In the title salt, $[C_{12}H_{14}N_2]^{2+}$, $2[IO_4]^-$, the cation is organized around an inversion center located at the centre of the CH_2CH_2 moiety and the two pyridine moieties are placed in *anti* positions with respect to each other. The I atom is in tetrahedral environment. Three O atoms of anion are involving in some C–H···O interactions with neighboring cations.

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The ability of quaternary ammonium cations to transfer the anionic reactants from aqueous media into organic media was discussed. The resultant effect is to increase the rate of the organic reaction by enhancing the reactivity of the anionic species and increasing the encounter rate with the organic substrate.[1] Periodic acid is a strong oxidant, and their salts such as some ammonium periodate compounds are frequently used to oxidize a variety of functional groups;[2-5] so, the application of periodate-based compounds in organic synthesis has been extensively reviewed.[6]

Here, we report on the synthesis and single crystal X-ray determination of the title salt; bis pyridinium 1,2-ethane periodate (Fig. 1). The initial substance ethane 1,2-bipyridinium dibromide, which was used for the preparation of title compound, was prepared from the following procedure: A solution of pyridnie (44.8 mmol) and 1,2-dibromoethane (22 mmol) in DMF (40 ml) was refluxed. After 2 h, the mixture was cooled and the produced white solid was filtered and washed with diethyl ether and dried. The title compound was prepared by the following method: To a solution of ethane 1,2-dipyridinum dibromide (10 mmol) in H_2O, a solution of KIO_4 (20 mmol) in H_2O was added and stirred. After 30 min, the precipitate was filtered and washed with H_2O. ^{1}H NMR (DMSO-d_6, 500.13 MHz, TMS, δ_{ppm}): 5.23 (s, 4H, 2CH2), 8.21 (t, 4H, Ar-H), 8.69 (t, 2H, Ar-H), 8.96 (d, 4H, Ar-H). ^{13}C NMR (DMSO-d_6, 125.76 MHz, TMS, δ_{ppm}): 60.63, 129.36, 146.18, 147.54. Selected data of IR spectrum (KBr, cm^{-1}): 3056, 1650, 888. Suitable single crystals for X-ray analysis were obtained from CH_3CN after slow evaporation at room temperature.

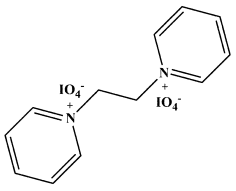

Fig. 1 Chemical diagram of the title compound.

X-ray crystallography investigation was performed at room temperature, and the crystallographic data are summarized in Table 1. Carbon-bound H-atoms were placed in calculated positions, C–H = 0.93 Å (aromatic) and 0.97 Å (CH_2), and were included in the refinement using a riding model approximation, with $U_{iso} = 1.2U_{eq}$(C). As the dication is organized at an inversion center located at the centre of CH_2CH_2 moiety, the asymmetric unit of title compound contains one half-dication and one periodate anion. The iodine atom is in tetrahedral

Table 1 Crystal data and structure refinement details for bis pyridinium 1,2-ethane periodate

Chemical formula: $C_{12}H_{14}I_2N_2O_8$	
Formula weight = 568.05	
T = 298(2)K	
Crystal system: Triclinic	Space group: $P\bar{1}$
a = 6.2405(12)Å	α = 100.02(3)°
b = 7.2635(15)Å	β = 94.59(3)°
c = 10.100(2)Å	γ = 100.02(3)°
V = 441.07(17)Å^3	Z = 1
D_x = 2.139 g/cm^3	
Radiation: Mo K_α (λ = 0.71073 Å)	
μ(Mo K_α) = 3.606 mm^{-1}	F(0 0 0) = 270
Crystal size = 0.38 × 0.3 × 0.15 mm^3	
No. of reflections collected = 4906	
No. of independent reflections = 2346	
θ range for data collection: 2.90 to 29.16°.	
Data/restraints/parameters = 2346/0/110	
Goodness-of-fit on F^2 = 1.164	
R indices [$I > 2\sigma(I)$]: R_1 = 0.0581, wR_2 = 0.1732	
R indices (all data): R_1 = 0.0772, wR_2 = 0.2452	
$(\Delta/\sigma)_{max}$ = 0.000	
$(\Delta\rho)_{max}$ = 2.481 eÅ^{-3}	$(\Delta\rho)_{min}$ = –3.852 eÅ^{-3}
Measurement: STOE IPDS II	
Program system: SHELXL-97[8]	
Structure determination: Direct method	
Refinement: Full-matrix least-squares on F^2	
CCDC deposition number: 821286	

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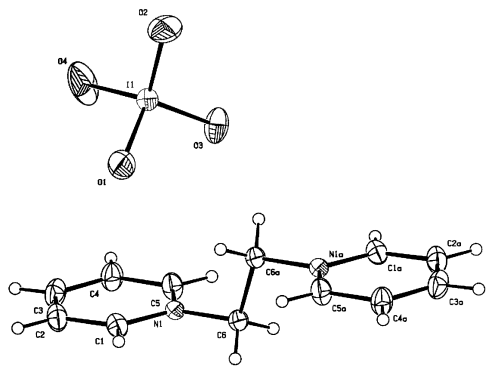

Fig. 2 Molecular view with the atom labeling scheme, displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

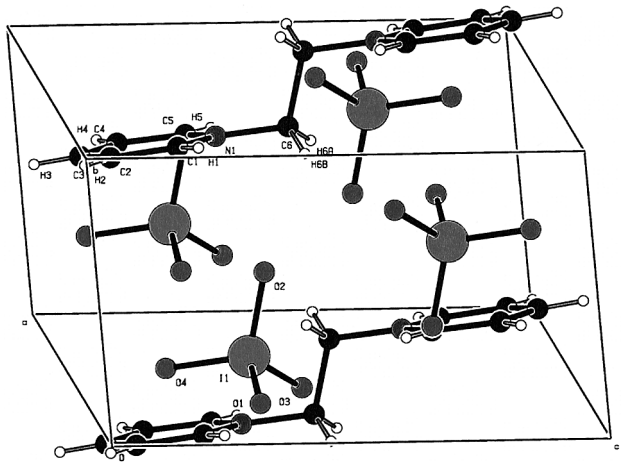

Fig. 3 Crystal structure of the molecule viewed along the *a*-axis.

environment (Fig. 2) with the bond angles in the range of 106.2(7)˚ to 112.4(5)˚. The I–O bond lengths are comparable to those in similar compounds like for example in $C_3H_{10}NO^+IO_4^-\cdot C_{12}H_{24}O_6$.[7] The two pyridine moieties are placed in *anti* positions to each other, this conformation of bis-pyridinium dication is similar to that found in 4 reported bis-pyridinium salts (CSD (version 5.32, updates Nov 2010);[9-12] however, there is only one report of different conformation.[13] Three O atoms of anion are involving in some C–H···O interactions (in the range of 3.011(14) to 3.393(14)Å) with four neighboring dications, Table 3. Moreover, each dication is interacted with eight anions *via* these non-covalent forces. A view of unit cell packing along the *a*-axis is shown in Fig. 3.

Table 2 Atomic coordinates (Å × 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for bis pyridinium 1,2-ethane periodate. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	$U_{(eq)}$
O(4)	793(17)	2320(30)	1328(10)	121(7)
O(2)	968(18)	5530(14)	3500(12)	79(3)
O(1)	-3030(12)	2826(16)	2643(10)	65(2)
O(3)	626(15)	1653(13)	3996(8)	59(2)
I(1)	-142(1)	3128(1)	2891(1)	38(1)
N(1)	4864(9)	8462(9)	3292(6)	30(1)
C(5)	6606(15)	7726(15)	2928(9)	43(2)
C(2)	3661(16)	8332(14)	982(9)	45(2)
C(3)	5481(19)	7552(14)	620(9)	47(2)
C(1)	3383(13)	8783(12)	2319(8)	38(2)
C(4)	6926(15)	7313(15)	1582(9)	45(2)
C(6)	4490(14)	8933(12)	4713(8)	37(2)

Table 3 Intermolecular interaction parameters (Å, ˚)

D-H···A	D-H	H···A	D···A	D-H···A
C1-H1…O3^{i}	0.9300	2.4200	3.265(12)	151.00
C2-H2…O4^{ii}	0.9300	2.5300	3.393(14)	155.00
C3-H3…O4^{iii}	0.9300	2.5300	3.163(16)	127.00
C5-H5…O3^{iv}	0.9300	2.5000	3.350(12)	148.00
C6-H6B…O2	0.9700	2.5000	3.011(14)	113.00

Symmetry codes: (i) *x*, 1+*y*, *z*; (ii) –*x*, 1–*y*, –*z*; (iii) 1–*x*, 1–*y*, –*z*; (iv) 1–*x*, 1–*y*, 1–*z*.

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