Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4,4′-Bipyridine-1,1′-diium 2,3,5,6-tetrabromoterephthalate dihydrate

Hitoshi Kumagai[a]* and Satoshi Kawata[b]

[a]Institute for Molecular Science, 38 Nishigounaka Okazaki, Aichi, Japan, and [b]Department of Chemistry, Fukuoka University, Fukuoka 814-0180, Japan
Correspondence e-mail: e1254@mosk.tytlabs.co.jp

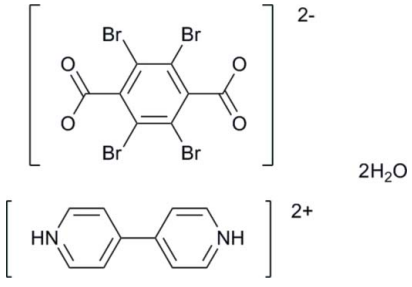
Received 9 July 2011; accepted 2 September 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.031; wR factor = 0.086; data-to-parameter ratio = 17.2.

The title compound, $C_{10}H_{10}N_2^{2+}\cdot C_8Br_4O_4^{2-}\cdot 2H_2O$, consists of a tetrabromoterephthalate dianion, a 4,4′-bipyridinium dication and two solvent water molecules. Crystallographic inversion centers are situated at the center of the aromatic ring of the dianion as well as at the midpoint of the carbon–carbon bond connecting the pyridine rings in the dication. In the crystal, intermolecular N—H···O hydrogen-bonding interactions between tetrabromoterephthalate dianions and protonated 4,4′-bipyridinium dications result in the formation of a chain-like structure. Further O—H···O hydrogen bonds between carboxylate O atoms and water molecules lead to the formation of a two-dimensional network in the crystal structure.

Related literature

For hydrogen-bonded assemblies, see: Desiraju & Steiner (1999); Jia *et al.* (2009); Soleimannejad *et al.* (2009). For proton transfer, see: Kawata *et al.* (2002).



Experimental

Crystal data

$C_{10}H_{10}N_2^{2+}\cdot C_8Br_4O_4^{2-}\cdot 2H_2O$ M_r = 673.93
Triclinic, $P\overline{1}$
a = 6.503 (3) Å
b = 9.249 (4) Å
c = 9.987 (4) Å
α = 64.119 (14)°
β = 85.868 (18)°
γ = 73.737 (14)°
V = 517.9 (4) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 7.83 mm^{-1}
T = 293 K
0.30 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury70 diffractometer
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.126, T_{max} = 0.209
5065 measured reflections
2336 independent reflections
2116 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.086
S = 1.19
2336 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −1.55 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H6···O2^{i}	0.963	1.944	2.822 (4)	150.5
O3—H7···O2	1.002	1.765	2.766 (3)	177.2
N1—H5···O1^{ii}	0.941	1.670	2.606 (4)	172.9

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x+1, y, z$.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *IL MILIONE* (Burla *et al.*, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2004); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010).

HK thanks the Japan Society for the Promotion of Science for his postdoctoral fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2306).

References

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D. & Spagna, R. (2007). *J. Appl. Cryst.* **40**, 609–613.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press Inc.
Jia, M., Liu, X., Miao, J., Xiong, W. & Chen, Z. (2009). *Acta Cryst.* E**65**, o2490.
Kawata, S., Adachi, K., Sugiyama, Y., Kabir, M. K. & Kaizaki, S. (2002). *CrystEngCommun*, **4**, 496–498.
Palmer, D. (2004). *CrystalMaker*. CrystalMaker Software Ltd, Yarnton, England.
Rigaku (1998). *REQAB*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2010). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Soleimannejad, J., Aghabozorg, H., Morsali, A., Hemmati, F. & Manteghi, F. (2009). *Acta Cryst.* E**65**, o153.

supporting information

Acta Cryst. (2011). E**67**, o2636 [https://doi.org/10.1107/S1600536811035926]

4,4′-Bipyridine-1,1′-diium 2,3,5,6-tetrabromoterephthalate dihydrate

Hitoshi Kumagai and Satoshi Kawata

S1. Comment

Hydrogen bonded inorganic and organic compounds are of great current interest in recent years due to fundamental scientific and technological applications (Desiraju & Steiner,1999; Kawata *et al.*, 2002). Here we report the synthesis and single-crystal structure of the title compound [$(C_8Br_4O_4)(C_{10}H_{10}N_2).2H_2O$)]. It consists of a tetrabromoterephthalate dianion, a 4,4′-bipyridinium dication and solvent water molecules. Intermolecular N–H···O hydrogen bonding interactions between tetrabromoterephthalate dianions and protonated 4,4′-bipyridinium dications result in the formation of a one-dimensional chain-like structure. Further O–H···O hydrogen bonds between oxygen atoms of carboxylates and water molecules lead to the formation of a two-dimensional network in the crystal structure.

S2. Experimental

An aqueous solution (2 ml) of cerium nitrate hexahydrate (0.43 g, 1 mmolL^{-1}) was transferred to a glass tube, then a mixture of tetrabromoterephthalic acid (0.48 g, 1 mmolL^{-1}), NaOH (0.08 g, 2 mmolL^{-1}) and 4,4′-bpy (0.15 g, 1 mmolL^{-1}) in ethanol/water (2 ml) was poured into the glass tube without mixing the two solutions. Colorless crystals began to form at ambient temperature during 1 month. One of these crystals was used for X-ray crystallography.

S3. Refinement

Hydrogen atoms bonded to carbon atoms, H1, H2, H3 and H4 were introduced at the positions calculated theoretically and refined using riding models with U_{iso}(H) = 1.5 U_{eq}(C). H5, H6, H7 are located in the Fourier difference maps but the positions of these atoms were not refined. Thermal parameteers have been fixed to 1.2 U_{eq}(N) or 1.5 U_{eq}(O), respectively.

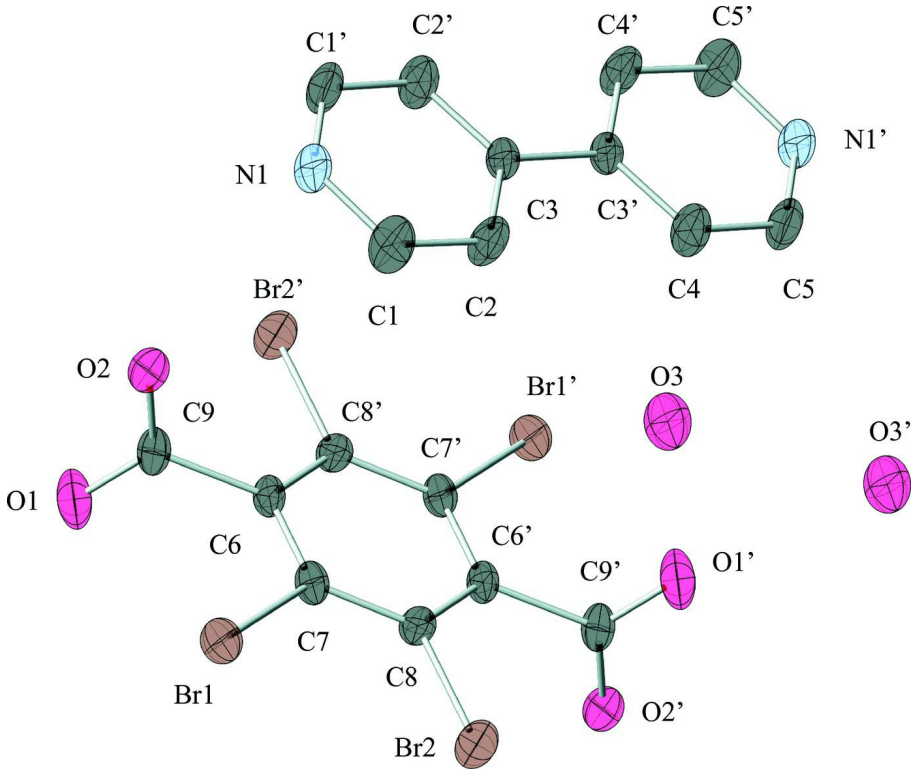


Figure 1

ORTEP drawing of the title compound showing 50% probability displacement ellipsoids.

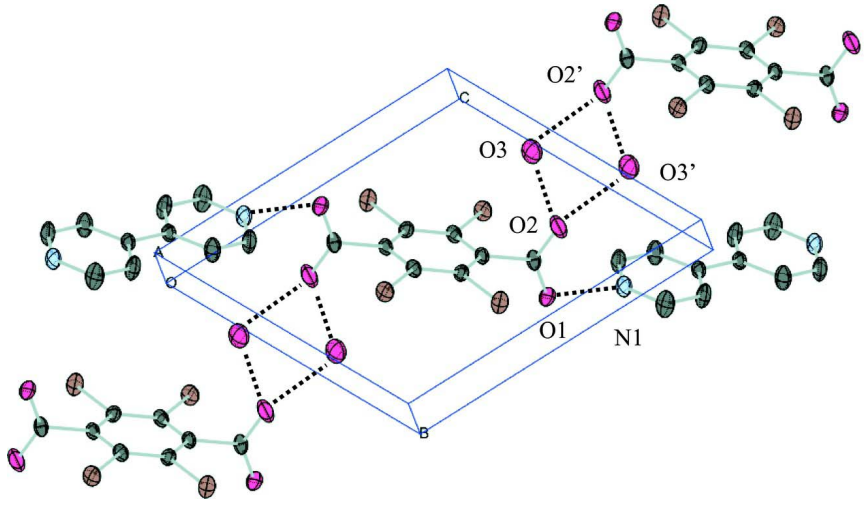


Figure 2

Hydrogen bonding interactions for the title compound.

4,4′-Bipyridine-1,1′-diium 2,3,5,6-tetrabromoterephthalate dihydrate

Crystal data

$C_{10}H_{10}N_2^{2+}\cdot C_8Br_4O_4^{2-}\cdot 2H_2O$
$M_r = 673.93$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.503$ (3) Å
$b = 9.249$ (4) Å
$c = 9.987$ (4) Å
$\alpha = 64.119$ (14)°
$\beta = 85.868$ (18)°
$\gamma = 73.737$ (14)°
$V = 517.9$ (4) Å^3
$Z = 1$
$F(000) = 324.00$
$D_x = 2.161$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
Cell parameters from 1137 reflections
$\theta = 3.3$–$27.5°$
$\mu = 7.83$ mm^{-1}
$T = 293$ K
Prism, colorless
0.30 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury70 diffractometer
Detector resolution: 7.314 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
$T_{min} = 0.126$, $T_{max} = 0.209$
5065 measured reflections
2336 independent reflections
2116 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$
$h = -8\rightarrow 8$
$k = -12\rightarrow 12$
$l = -12\rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.086$
$S = 1.19$
2336 reflections
136 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.1173P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -1.55$ e Å^{-3}

Special details

Geometry. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.10645 (4)	0.42116 (4)	0.71999 (3)	0.03083 (11)
Br2	0.32963 (5)	0.18104 (4)	0.54456 (3)	0.03350 (12)
O1	0.1557 (4)	0.8335 (3)	0.5839 (3)	0.0351 (5)
O2	0.3797 (4)	0.6584 (3)	0.7830 (3)	0.0422 (6)
O3	0.7487 (4)	0.4074 (3)	0.9249 (3)	0.0446 (6)
N1	0.8843 (4)	0.9226 (3)	0.7575 (3)	0.0306 (6)
C1	0.8549 (6)	1.0592 (5)	0.7789 (4)	0.0409 (8)

C2	0.7080 (5)	1.0919 (4)	0.8752 (4)	0.0368 (7)
C3	0.5825 (4)	0.9836 (4)	0.9480 (3)	0.0236 (6)
C4	0.6149 (5)	0.8444 (5)	0.9214 (4)	0.0367 (7)
C5	0.7679 (6)	0.8159 (4)	0.8268 (4)	0.0377 (7)
C6	0.4067 (4)	0.6003 (3)	0.5735 (3)	0.0221 (5)
C7	0.3331 (4)	0.4652 (4)	0.5922 (3)	0.0229 (5)
C8	0.4251 (4)	0.3656 (4)	0.5196 (3)	0.0231 (5)
C9	0.3056 (5)	0.7067 (4)	0.6539 (3)	0.0262 (6)
H1	0.9351	1.1338	0.7277	0.0491*
H2	0.6927	1.1859	0.8916	0.0442*
H3	0.5329	0.7698	0.9677	0.0441*
H4	0.7906	0.7208	0.8110	0.0452*
H5	0.9899	0.8937	0.6971	0.0367*
H6	0.7539	0.3878	1.0277	0.0670*
H7	0.6152	0.4970	0.8711	0.0670*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02820 (17)	0.03494 (19)	0.03224 (19)	−0.01138 (13)	0.01655 (12)	−0.01780 (14)
Br2	0.03620 (19)	0.03384 (19)	0.0411 (2)	−0.01650 (14)	0.01468 (14)	−0.02352 (15)
O1	0.0340 (11)	0.0330 (11)	0.0321 (11)	0.0036 (9)	0.0083 (9)	−0.0172 (9)
O2	0.0477 (13)	0.0549 (14)	0.0277 (12)	−0.0052 (11)	0.0025 (10)	−0.0266 (11)
O3	0.0460 (14)	0.0483 (14)	0.0416 (14)	−0.0126 (11)	0.0168 (11)	−0.0237 (12)
N1	0.0286 (12)	0.0356 (13)	0.0320 (13)	−0.0080 (10)	0.0150 (10)	−0.0211 (11)
C1	0.0426 (18)	0.0430 (18)	0.050 (2)	−0.0230 (15)	0.0297 (16)	−0.0292 (17)
C2	0.0434 (17)	0.0342 (16)	0.0468 (19)	−0.0185 (14)	0.0247 (15)	−0.0287 (15)
C3	0.0239 (13)	0.0270 (13)	0.0226 (13)	−0.0063 (10)	0.0070 (11)	−0.0145 (11)
C4	0.0438 (17)	0.0400 (16)	0.0412 (18)	−0.0220 (14)	0.0226 (15)	−0.0276 (15)
C5	0.0479 (18)	0.0391 (17)	0.0413 (18)	−0.0177 (14)	0.0192 (15)	−0.0302 (15)
C6	0.0204 (12)	0.0252 (12)	0.0200 (13)	−0.0012 (10)	0.0033 (10)	−0.0127 (11)
C7	0.0197 (12)	0.0283 (13)	0.0208 (13)	−0.0048 (10)	0.0067 (10)	−0.0127 (11)
C8	0.0225 (12)	0.0226 (12)	0.0245 (13)	−0.0046 (10)	0.0043 (10)	−0.0121 (11)
C9	0.0277 (14)	0.0307 (14)	0.0274 (15)	−0.0097 (11)	0.0122 (11)	−0.0196 (12)

Geometric parameters (Å, º)

Br1—C7	1.892 (3)	C6—C7	1.394 (5)
Br2—C8	1.887 (4)	C6—C8^{ii}	1.396 (4)
O1—C9	1.248 (3)	C6—C9	1.516 (5)
O2—C9	1.249 (4)	C7—C8	1.395 (5)
N1—C1	1.332 (6)	O3—H6	0.963
N1—C5	1.331 (5)	O3—H7	1.002
C1—C2	1.374 (6)	N1—H5	0.941
C2—C3	1.392 (5)	C1—H1	0.930
C3—C3^{i}	1.501 (4)	C2—H2	0.930
C3—C4	1.382 (6)	C4—H3	0.930
C4—C5	1.374 (5)	C5—H4	0.930

O1···H5^{iii}	1.670	H5···O1^{vi}	1.670
O1···H5^{iv}	2.828	H5···O1^{iv}	2.828
O2···H5^{iii}	2.737	H5···O2^{vi}	2.737
O2···H6^{v}	1.944	H6···O2^{v}	1.944
O2···H7	1.765	H7···O2	1.765

C1—N1—C5	120.5 (3)	C6^{ii}—C8—C7	120.4 (3)
N1—C1—C2	121.2 (4)	O1—C9—O2	126.8 (4)
C1—C2—C3	119.6 (4)	O1—C9—C6	116.2 (3)
C2—C3—C3^{i}	121.2 (4)	O2—C9—C6	116.9 (3)
C2—C3—C4	117.7 (3)	H6—O3—H7	110.0
C3^{i}—C3—C4	121.1 (3)	C1—N1—H5	122.8
C3—C4—C5	120.1 (4)	C5—N1—H5	116.6
N1—C5—C4	120.9 (4)	N1—C1—H1	119.417
C7—C6—C8^{ii}	118.8 (3)	C2—C1—H1	119.409
C7—C6—C9	120.1 (3)	C1—C2—H2	120.212
C8^{ii}—C6—C9	121.1 (3)	C3—C2—H2	120.215
Br1—C7—C6	117.8 (3)	C3—C4—H3	119.938
Br1—C7—C8	121.4 (3)	C5—C4—H3	119.934
C6—C7—C8	120.8 (3)	N1—C5—H4	119.564
Br2—C8—C6^{ii}	118.1 (3)	C4—C5—H4	119.572
Br2—C8—C7	121.6 (2)		

C1—N1—C5—C4	0.2 (5)	C8^{ii}—C6—C7—C8	−0.0 (4)
C5—N1—C1—C2	1.5 (5)	C7—C6—C9—O1	−93.1 (3)
N1—C1—C2—C3	−2.2 (5)	C7—C6—C9—O2	86.7 (4)
C1—C2—C3—C3^{i}	−178.9 (3)	C9—C6—C7—Br1	−0.1 (3)
C1—C2—C3—C4	1.1 (4)	C9—C6—C7—C8	−179.68 (19)
C2—C3—C3^{i}—C4^{i}	0.0 (4)	C8^{ii}—C6—C9—O1	87.3 (4)
C2—C3—C4—C5	0.5 (4)	C8^{ii}—C6—C9—O2	−93.0 (3)
C3^{i}—C3—C4—C5	−179.5 (3)	C9—C6—C8^{ii}—Br2^{ii}	−0.8 (3)
C4—C3—C3^{i}—C2^{i}	−0.0 (4)	C9—C6—C8^{ii}—C7^{ii}	179.68 (19)
C3—C4—C5—N1	−1.2 (5)	Br1—C7—C8—Br2	−0.1 (3)
C7—C6—C8^{ii}—Br2^{ii}	179.51 (18)	Br1—C7—C8—C6^{ii}	−179.58 (14)
C7—C6—C8^{ii}—C7^{ii}	0.0 (4)	C6—C7—C8—Br2	179.49 (18)
C8^{ii}—C6—C7—Br1	179.59 (18)	C6—C7—C8—C6^{ii}	0.0 (4)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, −*y*+2, −*z*+1; (v) −*x*+1, −*y*+1, −*z*+2; (vi) *x*+1, *y*, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H6···O2^{v}	0.963	1.944	2.822 (4)	150.5
O3—H7···O2	1.002	1.765	2.766 (3)	177.2
N1—H5···O1^{vi}	0.941	1.670	2.606 (4)	172.9

Symmetry codes: (v) −*x*+1, −*y*+1, −*z*+2; (vi) *x*+1, *y*, *z*.