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4,4′-[(2,7-Dibromofluorene-9,9-diyl)-dimethylene]dipyridinium bis(perchlorate)

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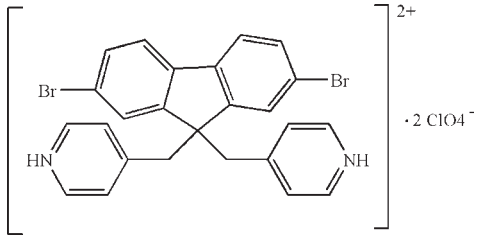
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.103; data-to-parameter ratio = 16.5.

In the crystal of the title compound, $C_{25}H_{20}Br_2N_2^{2+}\cdot 2ClO_4^-$, intermolecular N—H···O and C—H···O hydrogen bonds, along with C—H···π interactions, stabilize the crystal structure.

Related literature

A variety of ligands of different molecular dimensions and functional properties have been utilized in the preparation of numerous supramolecular assemblies with exotic architectures, see: Applegarth *et al.*, (2005). For related structures, see: Meerssche *et al.* (1979, 1980).



Experimental

Crystal data

$C_{25}H_{20}Br_2N_2^{2+}\cdot 2ClO_4^-$
M_r = 707.15
Monoclinic, $C2/c$
a = 15.605 (3) Å
b = 11.267 (2) Å
c = 16.318 (3) Å
β = 117.60 (3)°
V = 2542.6 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.45 mm^{-1}
T = 295 K
0.25 × 0.20 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.441, T_{max} = 0.537
11835 measured reflections
2915 independent reflections
2611 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
3 standard reflections every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.103
S = 1.06
2915 reflections
177 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}

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

*Cg*3 is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3	0.86	2.24	2.997 (3)	148
C11—H11A···O1	0.93	2.57	3.196 (3)	125
C12—H12A···O4^{i}	0.93	2.44	3.193 (3)	138
C13—H13A···O1^{ii}	0.93	2.47	3.376 (3)	164
C10—H10A···Cg3	0.93	2.93	3.688 (2)	140

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2685).

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supplementary materials

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4,4'-[(2,7-Dibromofluorene-9,9-diyl)dimethylene]dipyridinium bis(perchlorate)

Z. Xuan, S. Zhao, L. Lu, X. Wang and X. Yang

Comment

A variety of ligands of different molecular dimensions and functional properties were utilized for the preparation of numerous supramolecular assemblies of exotic architectures as reported in the recent literature (Applegarth *et al.*, 2005). Herein, we report a new bipyridine derivative of 2,7-dibromo-9,9-(4-pyridyl-methyl) fluorene [DBPMF].

scheme I

The structure of the title compound contains a protonated 2,7-dibromo-9,9-bis(4-pyridinium-methyl) fluorene dications $DBPMFH_2^{2+}$ and two perchlorate anions ClO_4^-. All the bond lengths and bond angles in the phenyl ring and five-membered ring are corresponding with those observed in 2-acetylaminofluorene (Meerssche *et al.*, 1980) and 4-acetylamino-fluorene (Meerssche *et al.*, 1979). Two bromine atoms along with the thirteen atoms of fluorenyl ring are coplanar (P1) and the biggest deviation is 0.038Å for C6 atom. The dihedral angle between the plane P1 and the pyridyl ring containing N1 atom is 72.11 (2)°.

In the crystal lattice, there are four types of supramolecular interactions (Table 1), including N—H···O hydrogen bonds, C—H···O potential hydrogen bonds, C—H···π supramolecular interaction and π–π stacking interactions. Among these supramolecular interactions, the two types N—H···O hydrogen bonds link two $DBPMFH_2^{2+}$ cations with two ClO_4^- anions to construct one-dimensional chains, then the other supramolecular interactions help the 1D chains to form three-dimensional net-works, which stabilize the crystal structure.

Experimental

DBPMF was synthesized by the reaction of 2,7-dibromofluorene (3.24 g, 0.01 mol) and 4-chloromethyl pyridine hydrochloride (1.64 g, 0.02 mol) in DMSO (70 ml). The title compound was obtained by the reaction of DBPMF (2.55 g, 5.0 mmol) and $HClO_4$ (0.26 ml, 5.0 mmol) in EtOH (50 ml). Single crystals suitable for x-ray measurements were obtained by recrystallization at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances=0.93-0.97 Å, N—H distance=0.86Å and with U_{iso}=1.2-1.5U_{eq}.

Figures

Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

4,4'-[(2,7-Dibromofluorene-9,9-diyl)dimethylene]dipyridinium bis(perchlorate)

Crystal data

$C_{25}H_{20}Br_2N_2^{2+}\cdot 2ClO_4^-$	$F(000) = 1408$
$M_r = 707.15$	$D_x = 1.847$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 25 reflections
$a = 15.605$ (3) Å	$\theta = 4$–$14°$
$b = 11.267$ (2) Å	$\mu = 3.45$ mm^{-1}
$c = 16.318$ (3) Å	$T = 295$ K
$\beta = 117.60$ (3)°	Block, yellow
$V = 2542.6$ (11) Å^3	0.25 × 0.20 × 0.18 mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	2611 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.062$
graphite	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
ω/2θ scans	$h = -20\rightarrow 20$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = -14\rightarrow 14$
$T_{min} = 0.441$, $T_{max} = 0.537$	$l = -21\rightarrow 21$
11835 measured reflections	3 standard reflections every 100 reflections
2915 independent reflections	intensity decay: none

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.039$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.5103P]$ where $P = (F_o^2 + 2F_c^2)/3$
2915 reflections	$(\Delta/\sigma)_{max} = 0.001$
177 parameters	$\Delta\rho_{max} = 1.01$ e Å^{-3}

0 restraints $\Delta\rho_{min} = -0.79$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	−0.201221 (15)	0.319251 (18)	−0.114789 (15)	0.01844 (12)
N1	0.33006 (13)	0.39368 (16)	0.24329 (14)	0.0178 (4)
H1A	0.3819	0.3707	0.2418	0.021*
C1	−0.13197 (15)	0.2901 (2)	0.01439 (16)	0.0153 (4)
C2	−0.11455 (16)	0.17300 (17)	0.04368 (17)	0.0162 (5)
H2A	−0.1377	0.1115	0.0009	0.019*
C3	−0.06207 (15)	0.14838 (19)	0.13788 (15)	0.0154 (4)
H3A	−0.0500	0.0704	0.1589	0.019*
C4	−0.02836 (14)	0.24228 (18)	0.19940 (15)	0.0140 (4)
C5	−0.04692 (14)	0.36049 (18)	0.16834 (16)	0.0141 (4)
C6	−0.09989 (14)	0.38606 (18)	0.07490 (15)	0.0146 (4)
H6A	−0.1134	0.4638	0.0536	0.017*
C7	0.0000	0.4457 (2)	0.2500	0.0123 (5)
C8	0.07543 (14)	0.52981 (17)	0.24235 (15)	0.0136 (4)
H8A	0.0429	0.5737	0.1849	0.016*
H8B	0.0965	0.5870	0.2924	0.016*
C9	0.16421 (14)	0.47237 (18)	0.24518 (15)	0.0133 (4)
C10	0.16000 (15)	0.39694 (18)	0.17545 (15)	0.0157 (4)
H10A	0.1004	0.3722	0.1290	0.019*
C11	0.24415 (15)	0.35912 (19)	0.17540 (16)	0.0175 (4)
H11A	0.2413	0.3098	0.1285	0.021*
C12	0.33797 (15)	0.46320 (19)	0.31370 (16)	0.0183 (4)
H12A	0.3986	0.4841	0.3605	0.022*
C13	0.25553 (15)	0.50303 (18)	0.31584 (15)	0.0152 (4)
H13A	0.2606	0.5505	0.3645	0.018*
Cl1	0.41022 (4)	0.31707 (4)	0.05644 (4)	0.01488 (15)
O1	0.31184 (11)	0.35890 (17)	0.01812 (12)	0.0258 (4)
O2	0.41264 (16)	0.19359 (15)	0.03767 (15)	0.0321 (5)
O3	0.45717 (12)	0.33505 (14)	0.15648 (12)	0.0213 (4)
O4	0.46088 (12)	0.38494 (16)	0.01772 (12)	0.0286 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02330 (17)	0.01761 (16)	0.01334 (17)	−0.00066 (7)	0.00760 (12)	−0.00009 (7)
N1	0.0150 (8)	0.0174 (9)	0.0236 (10)	0.0018 (7)	0.0112 (8)	0.0021 (8)
C1	0.0146 (9)	0.0182 (9)	0.0130 (10)	−0.0009 (8)	0.0064 (8)	0.0001 (9)
C2	0.0211 (11)	0.0122 (10)	0.0171 (12)	−0.0033 (7)	0.0105 (10)	−0.0052 (8)
C3	0.0200 (10)	0.0111 (9)	0.0167 (11)	0.0006 (8)	0.0097 (9)	0.0000 (9)
C4	0.0152 (9)	0.0124 (9)	0.0165 (11)	0.0002 (7)	0.0090 (8)	0.0018 (8)
C5	0.0144 (9)	0.0106 (9)	0.0196 (11)	−0.0009 (7)	0.0097 (8)	−0.0020 (9)
C6	0.0158 (9)	0.0119 (9)	0.0171 (10)	−0.0002 (7)	0.0086 (8)	0.0008 (8)
C7	0.0125 (12)	0.0115 (13)	0.0135 (14)	0.000	0.0064 (11)	0.000
C8	0.0160 (9)	0.0095 (8)	0.0167 (10)	−0.0007 (7)	0.0088 (8)	0.0001 (8)
C9	0.0162 (9)	0.0108 (9)	0.0152 (10)	−0.0005 (7)	0.0091 (8)	0.0032 (8)
C10	0.0165 (9)	0.0158 (10)	0.0154 (10)	−0.0007 (8)	0.0079 (8)	0.0000 (8)
C11	0.0207 (10)	0.0148 (10)	0.0201 (12)	0.0005 (8)	0.0121 (9)	0.0000 (9)
C12	0.0153 (9)	0.0183 (10)	0.0184 (11)	−0.0014 (8)	0.0054 (8)	0.0019 (9)
C13	0.0181 (10)	0.0134 (9)	0.0135 (10)	−0.0010 (8)	0.0068 (8)	0.0017 (8)
Cl1	0.0145 (3)	0.0161 (3)	0.0132 (3)	−0.00181 (16)	0.0057 (2)	−0.00099 (17)
O1	0.0162 (8)	0.0345 (9)	0.0247 (9)	0.0037 (7)	0.0077 (7)	0.0074 (8)
O2	0.0390 (10)	0.0178 (9)	0.0283 (11)	−0.0006 (7)	0.0061 (9)	−0.0061 (7)
O3	0.0210 (8)	0.0273 (8)	0.0128 (8)	−0.0003 (6)	0.0055 (7)	−0.0034 (7)
O4	0.0253 (8)	0.0390 (10)	0.0264 (9)	−0.0070 (7)	0.0161 (7)	0.0037 (8)

Geometric parameters (Å, °)

Br1—C1	1.900 (2)	C7—C8	1.561 (2)
N1—C11	1.342 (3)	C8—C9	1.510 (3)
N1—C12	1.348 (3)	C8—H8A	0.9700
N1—H1A	0.8600	C8—H8B	0.9700
C1—C2	1.387 (3)	C9—C10	1.397 (3)
C1—C6	1.392 (3)	C9—C13	1.399 (3)
C2—C3	1.394 (3)	C10—C11	1.381 (3)
C2—H2A	0.9300	C10—H10A	0.9300
C3—C4	1.384 (3)	C11—H11A	0.9300
C3—H3A	0.9300	C12—C13	1.378 (3)
C4—C5	1.407 (3)	C12—H12A	0.9300
C4—C4^{i}	1.468 (4)	C13—H13A	0.9300
C5—C6	1.387 (3)	Cl1—O2	1.4289 (18)
C5—C7	1.526 (3)	Cl1—O4	1.4395 (17)
C6—H6A	0.9300	Cl1—O1	1.4423 (16)
C7—C5^{i}	1.526 (3)	Cl1—O3	1.4609 (19)
C7—C8^{i}	1.561 (2)		
C11—N1—C12	122.30 (19)	C9—C8—C7	116.89 (17)
C11—N1—H1A	118.9	C9—C8—H8A	108.1
C12—N1—H1A	118.9	C7—C8—H8A	108.1
C2—C1—C6	123.1 (2)	C9—C8—H8B	108.1

C2—C1—Br1	117.84 (18)	C7—C8—H8B	108.1
C6—C1—Br1	119.06 (17)	H8A—C8—H8B	107.3
C1—C2—C3	119.4 (2)	C10—C9—C13	117.85 (19)
C1—C2—H2A	120.3	C10—C9—C8	122.64 (18)
C3—C2—H2A	120.3	C13—C9—C8	119.28 (19)
C4—C3—C2	118.7 (2)	C11—C10—C9	120.1 (2)
C4—C3—H3A	120.7	C11—C10—H10A	119.9
C2—C3—H3A	120.7	C9—C10—H10A	119.9
C3—C4—C5	121.1 (2)	N1—C11—C10	119.8 (2)
C3—C4—C4^{i}	130.12 (13)	N1—C11—H11A	120.1
C5—C4—C4^{i}	108.75 (13)	C10—C11—H11A	120.1
C6—C5—C4	120.7 (2)	N1—C12—C13	119.5 (2)
C6—C5—C7	129.05 (19)	N1—C12—H12A	120.2
C4—C5—C7	110.21 (19)	C13—C12—H12A	120.2
C5—C6—C1	117.00 (19)	C12—C13—C9	120.3 (2)
C5—C6—H6A	121.5	C12—C13—H13A	119.8
C1—C6—H6A	121.5	C9—C13—H13A	119.8
C5—C7—C5^{i}	102.1 (2)	O2—Cl1—O4	110.40 (13)
C5—C7—C8^{i}	112.17 (11)	O2—Cl1—O1	110.72 (12)
C5^{i}—C7—C8^{i}	112.75 (11)	O4—Cl1—O1	109.07 (11)
C5—C7—C8	112.75 (11)	O2—Cl1—O3	108.98 (11)
C5^{i}—C7—C8	112.17 (11)	O4—Cl1—O3	108.89 (10)
C8^{i}—C7—C8	105.2 (2)	O1—Cl1—O3	108.74 (11)

Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

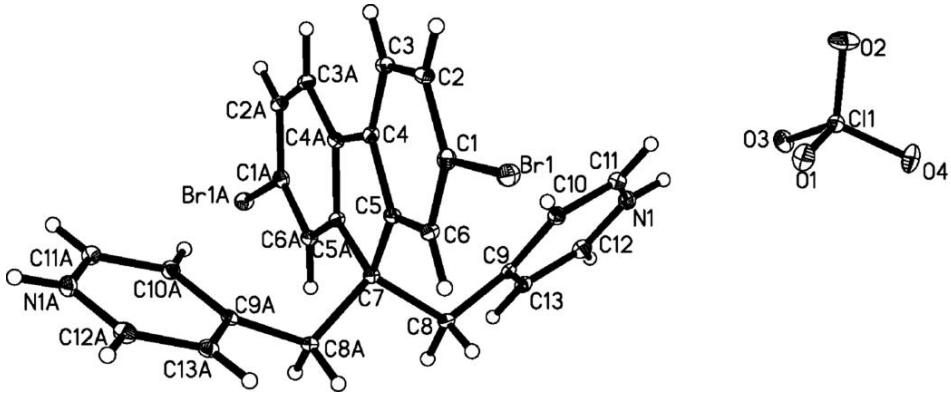
Hydrogen-bond geometry (Å, °)

Cg3 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O3	0.86	2.24	2.997 (3)	148.
C11—H11A···O1	0.93	2.57	3.196 (3)	125.
C12—H12A···O4^{ii}	0.93	2.44	3.193 (3)	138.
C13—H13A···O1^{iii}	0.93	2.47	3.376 (3)	164.
C10—H10A···Cg3	0.93	2.93	3.688 (2)	140.

Symmetry codes: (ii) −*x*+1, *y*, −*z*+1/2; (iii) *x*, −*y*+1, *z*+1/2.

Fig. 1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C4
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C10
N1
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C9
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O3
O1
O4