

***N,N'*-[1,4-Phenylenebis(methylene)]bis-*(N,N*-diethylethanaminium) dibromide**Munirah Sufiyah Abdul Rahim,<sup>a</sup> Hamid Khaledi,<sup>b\*</sup> Yatimah Alias<sup>a</sup> and Urs Welz-Biermann<sup>c</sup><sup>a</sup>University of Malaya Centre for Ionic Liquids, Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, <sup>b</sup>Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and <sup>c</sup>China Ionic Liquid Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023 Dalian, People's Republic of China

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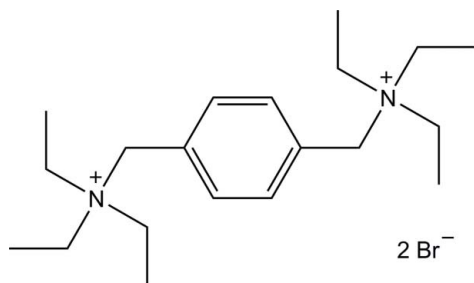
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.017;  $wR$  factor = 0.043; data-to-parameter ratio = 20.6.

In the crystal structure of the title compound,  $\text{C}_{20}\text{H}_{38}\text{N}_2^{2+} \cdot 2\text{Br}^-$ , the centroid of the aromatic ring is located on an inversion center, so that the asymmetric unit consists of one-half molecule of the dication and one bromide anion.  $\text{C}-\text{H} \cdots \text{Br}$  interactions connect the two components into a three-dimensional network. An intramolecular  $\text{C}-\text{H} \cdots \pi$  interaction is also observed.

**Related literature**

For the properties of dicationic ionic liquids, see: Anderson *et al.* (2005). For the structure of *p*-phenylenedimethanaminium dibromide, see: Zhang & Han (2010).

**Experimental***Crystal data* $\text{C}_{20}\text{H}_{38}\text{N}_2^{2+} \cdot 2\text{Br}^-$  $M_r = 466.34$ 

Monoclinic,  $P2_1/n$   
 $a = 8.2713$  (5) Å  
 $b = 14.1440$  (9) Å  
 $c = 9.0762$  (6) Å  
 $\beta = 97.634$  (1)°  
 $V = 1052.41$  (12) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 3.86$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.51 \times 0.47 \times 0.35$  mm

*Data collection*

Bruker APEXII CCD  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.244$ ,  $T_{\max} = 0.346$

10066 measured reflections  
 2304 independent reflections  
 2093 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.017$   
 $wR(F^2) = 0.043$   
 $S = 1.06$   
 2304 reflections

112 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.43$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.23$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

Cg is the centroid of the aromatic ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C7}-\text{H7A} \cdots \text{Br1}$	0.99	2.80	3.7565 (14)	163
$\text{C2}-\text{H2B} \cdots \text{Br1}^i$	0.99	2.90	3.7716 (14)	148
$\text{C6}-\text{H6B} \cdots \text{Br1}^{ii}$	0.99	2.92	3.8318 (14)	153
$\text{C7}-\text{H7B} \cdots \text{Br1}^{ii}$	0.99	2.89	3.7832 (14)	150
$\text{C1}-\text{H1C} \cdots \text{Cg}$	0.98	2.74	3.6529 (16)	156

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: SHELXL97 and publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5042).

**References**

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**supplementary materials**

*Acta Cryst.* (2012). E68, o369 [ doi:10.1107/S1600536812000141 ]

***N,N'*-[1,4-Phenylenebis(methylene)]bis(*N,N*-diethylethanaminium) dibromide**

**M. S. Abdul Rahim, H. Khaledi, Y. Alias and U. Welz-Biermann**

**Comment**

In comparison to the common singly charged ionic liquids, dicationic ionic liquids are a new class of organic salts having two positive charges on the same cation. They have been proved to have a better performance in terms of thermal stability, wide liquidus range, and unusual dissolution properties (Anderson *et al.*, 2005). The title compound was synthesized as a precursor for the synthesis of dicationic ionic liquids with a rigid phenylene group spacer.

Similar to the structure of *p*-phenylenedimethanaminium dibromide (Zhang & Han, 2010), the centroid of the aromatic ring is located on an inversion center, therefore the asymmetric unit consists of one-half of the dication and one bromide anion. In the crystal, the cations and anions are linked into a three-dimensional polymeric structure *via* C—H···Br interactions. The network is further consolidated by intramolecular C—H··· $\pi$  interactions (Table 1).

**Experimental**

Triethylamine (3.06 ml, 22 mmol) was added dropwise to a solution of  $\alpha,\alpha$ -dibromo-*p*-xylene (2.64 g, 10 mmol) in acetonitrile (50 ml). The mixture was stirred at room temperature for 24 hr. The white precipitate of the product was filtered and washed with acetonitrile and dried under vacuum. Recrystallization of the dicationic salt from methanol afforded crystals suitable for X-ray crystallographic analysis

**Refinement**

H atoms were placed at calculated positions and refined as riding atoms, with C—H distances of 0.95 (aryl), 0.98 (methyl) and 0.99 (methylene) Å, and with  $U_{iso}(H)$  set to 1.2 (1.5 for methyl)  $U_{eq}(C)$ .

**Figures**

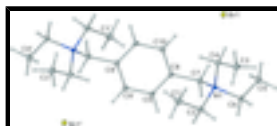


Fig. 1. Molecular structure of the title compound with displacement ellipsoids drawn at 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. [Symmetry code: ' = -x + 1, -y + 1, -z + 1.]

***N,N'*-[1,4-Phenylenebis(methylene)]bis(*N,N*- diethylethanaminium) dibromide**

*Crystal data*

$C_{20}H_{38}N_2^{2+} \cdot 2Br^-$

$M_r = 466.34$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$F(000) = 484$

$D_x = 1.472 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8155 reflections

# supplementary materials

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$a = 8.2713 (5) \text{ \AA}$	$\theta = 2.7\text{--}28.3^\circ$
$b = 14.1440 (9) \text{ \AA}$	$\mu = 3.86 \text{ mm}^{-1}$
$c = 9.0762 (6) \text{ \AA}$	$T = 100 \text{ K}$
$\beta = 97.634 (1)^\circ$	Block, colorless
$V = 1052.41 (12) \text{ \AA}^3$	$0.51 \times 0.47 \times 0.35 \text{ mm}$
$Z = 2$	

## Data collection

Bruker APEXII CCD diffractometer	2304 independent reflections
Radiation source: fine-focus sealed tube graphite	2093 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.021$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 27.0^\circ$ , $\theta_{\text{min}} = 2.7^\circ$
$T_{\text{min}} = 0.244$ , $T_{\text{max}} = 0.346$	$h = -10 \rightarrow 10$
10066 measured reflections	$k = -16 \rightarrow 18$
	$l = -11 \rightarrow 11$

## Refinement

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.017$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.043$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 0.5002P]$
2304 reflections	where $P = (F_o^2 + 2F_c^2)/3$
112 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

## Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 ( $\text{\AA}^2$ )

$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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N1	0.82236 (14)	0.33100 (8)	0.70235 (13)	0.0099 (2)
C1	0.72184 (18)	0.46030 (11)	0.87038 (16)	0.0176 (3)
H1A	0.8299	0.4897	0.8894	0.026*
H1B	0.6651	0.4681	0.9578	0.026*
H1C	0.6585	0.4906	0.7843	0.026*
C2	0.74049 (18)	0.35590 (10)	0.83906 (15)	0.0138 (3)
H2A	0.6308	0.3267	0.8271	0.017*
H2B	0.8045	0.3266	0.9273	0.017*
C3	1.10397 (18)	0.38839 (11)	0.80909 (16)	0.0156 (3)
H3A	1.0615	0.3870	0.9049	0.023*
H3B	1.1769	0.4428	0.8062	0.023*
H3C	1.1644	0.3300	0.7967	0.023*
C4	0.96263 (16)	0.39682 (10)	0.68396 (15)	0.0120 (3)
H4A	0.9223	0.4628	0.6796	0.014*
H4B	1.0028	0.3828	0.5883	0.014*
C5	0.97084 (18)	0.18930 (11)	0.60528 (17)	0.0166 (3)
H5A	0.8954	0.1845	0.5127	0.025*
H5B	1.0132	0.1264	0.6346	0.025*
H5C	1.0616	0.2311	0.5900	0.025*
C6	0.88154 (17)	0.22941 (10)	0.72681 (16)	0.0131 (3)
H6A	0.9550	0.2263	0.8221	0.016*
H6B	0.7862	0.1887	0.7364	0.016*
C7	0.69822 (17)	0.33096 (10)	0.56112 (15)	0.0113 (3)
H7A	0.7577	0.3197	0.4750	0.014*
H7B	0.6231	0.2770	0.5668	0.014*
C8	0.59739 (16)	0.41916 (10)	0.53110 (15)	0.0110 (3)
C9	0.43874 (17)	0.42236 (10)	0.56832 (15)	0.0124 (3)
H9	0.3958	0.3692	0.6139	0.015*
C10	0.65646 (17)	0.49722 (10)	0.46095 (15)	0.0126 (3)
H10	0.7630	0.4954	0.4329	0.015*
Br1	0.937757 (16)	0.344754 (10)	0.237945 (15)	0.01420 (6)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0107 (5)	0.0084 (6)	0.0103 (5)	0.0003 (5)	-0.0002 (4)	0.0017 (4)
C1	0.0219 (7)	0.0177 (8)	0.0136 (7)	0.0005 (6)	0.0034 (6)	-0.0040 (6)
C2	0.0152 (7)	0.0164 (7)	0.0102 (6)	-0.0006 (6)	0.0035 (5)	-0.0001 (5)
C3	0.0136 (7)	0.0160 (8)	0.0162 (7)	-0.0026 (6)	-0.0022 (5)	0.0011 (6)
C4	0.0126 (6)	0.0107 (7)	0.0126 (6)	-0.0029 (5)	0.0009 (5)	0.0008 (5)
C5	0.0162 (7)	0.0118 (7)	0.0212 (7)	0.0033 (6)	0.0005 (6)	-0.0012 (6)
C6	0.0137 (6)	0.0089 (7)	0.0160 (7)	0.0011 (6)	-0.0007 (5)	0.0034 (6)
C7	0.0111 (6)	0.0112 (7)	0.0108 (6)	-0.0007 (5)	-0.0020 (5)	-0.0008 (5)
C8	0.0122 (6)	0.0105 (7)	0.0095 (6)	0.0009 (5)	-0.0017 (5)	-0.0005 (5)
C9	0.0132 (6)	0.0115 (7)	0.0124 (6)	-0.0013 (5)	0.0011 (5)	0.0029 (5)
C10	0.0106 (6)	0.0149 (7)	0.0121 (6)	0.0001 (5)	0.0012 (5)	0.0006 (5)
Br1	0.01526 (8)	0.01314 (8)	0.01435 (8)	0.00247 (5)	0.00246 (5)	0.00042 (5)

## supplementary materials

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### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

N1—C4	1.5140 (17)	C5—C6	1.517 (2)
N1—C6	1.5246 (18)	C5—H5A	0.9800
N1—C2	1.5314 (17)	C5—H5B	0.9800
N1—C7	1.5322 (17)	C5—H5C	0.9800
C1—C2	1.516 (2)	C6—H6A	0.9900
C1—H1A	0.9800	C6—H6B	0.9900
C1—H1B	0.9800	C7—C8	1.5052 (19)
C1—H1C	0.9800	C7—H7A	0.9900
C2—H2A	0.9900	C7—H7B	0.9900
C2—H2B	0.9900	C8—C10	1.395 (2)
C3—C4	1.5225 (19)	C8—C9	1.3986 (19)
C3—H3A	0.9800	C9—C10 <sup>i</sup>	1.389 (2)
C3—H3B	0.9800	C9—H9	0.9500
C3—H3C	0.9800	C10—C9 <sup>i</sup>	1.389 (2)
C4—H4A	0.9900	C10—H10	0.9500
C4—H4B	0.9900		
C4—N1—C6	111.08 (10)	H4A—C4—H4B	107.8
C4—N1—C2	112.07 (11)	C6—C5—H5A	109.5
C6—N1—C2	105.47 (10)	C6—C5—H5B	109.5
C4—N1—C7	110.25 (10)	H5A—C5—H5B	109.5
C6—N1—C7	106.74 (10)	C6—C5—H5C	109.5
C2—N1—C7	111.01 (10)	H5A—C5—H5C	109.5
C2—C1—H1A	109.5	H5B—C5—H5C	109.5
C2—C1—H1B	109.5	C5—C6—N1	115.13 (12)
H1A—C1—H1B	109.5	C5—C6—H6A	108.5
C2—C1—H1C	109.5	N1—C6—H6A	108.5
H1A—C1—H1C	109.5	C5—C6—H6B	108.5
H1B—C1—H1C	109.5	N1—C6—H6B	108.5
C1—C2—N1	116.30 (12)	H6A—C6—H6B	107.5
C1—C2—H2A	108.2	C8—C7—N1	116.41 (11)
N1—C2—H2A	108.2	C8—C7—H7A	108.2
C1—C2—H2B	108.2	N1—C7—H7A	108.2
N1—C2—H2B	108.2	C8—C7—H7B	108.2
H2A—C2—H2B	107.4	N1—C7—H7B	108.2
C4—C3—H3A	109.5	H7A—C7—H7B	107.3
C4—C3—H3B	109.5	C10—C8—C9	118.77 (13)
H3A—C3—H3B	109.5	C10—C8—C7	121.29 (12)
C4—C3—H3C	109.5	C9—C8—C7	119.88 (13)
H3A—C3—H3C	109.5	C10 <sup>i</sup> —C9—C8	120.44 (13)
H3B—C3—H3C	109.5	C10 <sup>i</sup> —C9—H9	119.8
N1—C4—C3	113.17 (11)	C8—C9—H9	119.8
N1—C4—H4A	108.9	C9 <sup>i</sup> —C10—C8	120.76 (13)
C3—C4—H4A	108.9	C9 <sup>i</sup> —C10—H10	119.6
N1—C4—H4B	108.9	C8—C10—H10	119.6
C3—C4—H4B	108.9		

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

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

*Cg* is the centroid of the aromatic ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C7—H7A $\cdots$ Br1	0.99	2.80	3.7565 (14)	163.
C2—H2B $\cdots$ Br1 <sup>ii</sup>	0.99	2.90	3.7716 (14)	148.
C6—H6B $\cdots$ Br1 <sup>iii</sup>	0.99	2.92	3.8318 (14)	153.
C7—H7B $\cdots$ Br1 <sup>iii</sup>	0.99	2.89	3.7832 (14)	150.
C1—H1C $\cdots$ Cg	0.98	2.74	3.6529 (16)	156

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

Fig. 1

