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# Effect of methylene *versus* ethylene linkers on structural properties of *tert*-butyl and mesityl bis(imidazolium) bromide salts

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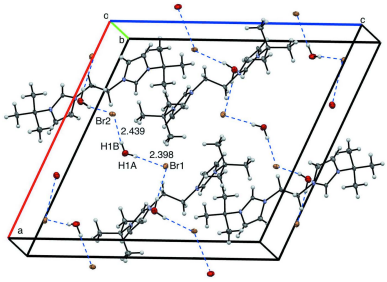
The crystal structures of ligand precursor bis(imidazolium) salts 1,1′-methylenebis(3-*tert*-butylimidazolium) dibromide monohydrate, $C_{15}H_{26}N_4^{+}\cdot 2Br^{-}\cdot H_2O$ or $[^{tBu}NHC_2Me][Br]_2\cdot H_2O$, 1,1′-(ethane-1,2-diyl)bis(3-*tert*-butylimidazolium) dibromide dihydrate, $C_{16}H_{28}N_4^{+}\cdot 2Br^{-}\cdot 2H_2O$ or $[^{tBu}NHC_2Et][Br]_2\cdot 2H_2O$, 1,1′-methylenebis[3-(2,4,6-trimethylphenyl)imidazolium] dibromide dihydrate, $C_{25}H_{30}N_4^{2+}\cdot 2Br^{-}\cdot 2H_2O$ or $[^{Mes}NHC_2Me][Br]_2\cdot 2H_2O$, and 1,1′-(ethane-1,2-diyl)bis[3-(2,4,6-trimethylphenyl)imidazolium] dibromide tetrahydrate, $C_{26}H_{32}N_4^{2+}\cdot 2Br^{-}\cdot 4H_2O$ or $[^{Mes}NHC_2Et][Br]_2\cdot 4H_2O$, are reported. At 293 K, $[^{tBu}NHC_2Me][Br]_2\cdot H_2O$ crystallizes in the $P2_1/c$ space group, while $[^{tBu}NHC_2Et][Br]_2\cdot 2H_2O$ crystallizes in the $P2_1/n$ space group at 100 K. At 112 K, $[^{Mes}NHC_2Me][Br]_2\cdot 2H_2O$ crystallizes in the orthorhombic space group *Pccn* while $[^{Mes}NHC_2Et][Br]_2\cdot 4H_2O$ crystallizes in the $P2_1/c$ space group at 100 K. Bond distances and angles within the imidazolium rings are generally comparable among the four structures. All four bis(imidazolium) salts co-crystallize with one to four molecules of water.

## 1. Chemical context

Bis(imidazolium) salts are common precursors for the synthesis of bidentate *N*-heterocyclic carbene ($NHC_2$) ligands, which can be used to stabilize a variety of metal complexes and catalysts. Bis(imidazolium) salts, $[^{R}NHC_2R^{1}][X]_2$ are relatively modular in that modifications can be relatively easily made to exterior groups attached to each NHC ($R$), the moiety linking the two NHC groups ($R^1$), and the counter-ion ($X$). One general synthetic approach for synthesizing bis(imidazolium) salts is where two equivalents of an alkyl or aryl imidazole are combined with one equivalent of an organic dihalide reagent and refluxed to afford the final product (Gardiner *et al.*, 1999). A simplified procedure for a variety of ligand salts using pressure tubes resulting in yields that were generally over 80% was also reported (Scherg *et al.*, 2006). Some reports have gone even further to minimize solvent in the synthesis of these ligand precursors, including a solvent-free synthesis (Cao *et al.*, 2011, 2012). This implies that the exterior $R$ groups can easily be modified by changing the alkyl or aryl group on the starting imidazole. The linking group $R^1$ and counter-ion $X$ can be modified by changing the organic dihalide reagent. In this fashion, a library of bis(imidazolium) salts can be relatively easily synthesized from alkyl or aryl imidazoles, and some are also commercially available.

Some of the most widely reported bis(imidazolium) salts are those with *tert*-butyl ($^t$Bu) and mesityl (Mes) exterior $R$ groups

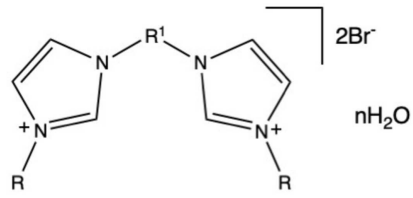


and methylene (Me) or ethylene (Et) linking $R^1$ groups. [$^{Mes}$NHC$_2$Et][Br]$_2$ was even reported to be a stand-alone catalyst for the conversion of arylaldehydes to carboxylic acids in combination with water and $K_2CO_3$ in DMSO (Yang *et al.*, 2013). Methylene linkers are quite commonly used for complexing to metals, and although examples with ethylene linkers are fewer, comparative studies report that changing the linker affects catalysis. For example, shorter methylene linkers ($R^1$) were reported to be more effective for hydrosilylation reactions with Rh$^I$ complexes than ethylene linkers (Riederer *et al.*, 2010).

The bidentate NHC ligand system is highly versatile for stabilizing a range of metals, some of which result in catalytically active systems. For example, [$^{tBu}$NHC$_2$Me][Br]$_2$ and [$^{tBu}$NHC$_2$Et][Br]$_2$ were used as precursors for synthesis of rhodium complexes (Leung *et al.*, 2006). [$^{tBu}$NHC$_2$Et][Cl]$_2$ was used for synthesis of aluminum, gallium, and indium complexes (Baker *et al.*, 2002). [$^{Mes}$NHC$_2$Et][Br]$_2$ was reported for synthesizing rhenium complexes (Hock *et al.*, 2014; Hiltner *et al.*, 2010), palladium complexes *via* Pd(OAc)$_2$-assisted deprotometalation (Wierenga *et al.*, 2019), palladium complexes *via* silver transmetallation (Sluijter *et al.*, 2013), and for palladium catalysts for Suzuki and Heck coupling reactions (Lee *et al.*, 2004). Other reported palladium complexes were active for dehalogenation of aryl halides (Viciu *et al.*, 2001).

Examples with first row transition metals are fewer, with nickel being the most commonly reported. Nickel carbonato complexes were synthesized with [$^{Mes}$NHC$_2$Me][Cl]$_2$ and [$^{Mes}$NHC$_2$Et][Cl]$_2$ ligand precursors (Guo *et al.*, 2013). Iron complexes for use in aryl Grignard-alkyl halide cross-coupling reactions were synthesized using various bis(imidazolium) salts including [$^{tBu}$NHC$_2$Me][Cl]$_2$, [$^{tBu}$NHC$_2$Me][Br]$_2$, [$^{Mes}$NHC$_2$Me][Cl]$_2$, [$^{Mes}$NHC$_2$Me][Br]$_2$, and [$^{Mes}$NHC$_2$Et][Br]$_2$ (Meyer *et al.*, 2011).

When used for stabilizing bimetallic systems, [$^{tBu}$NHC$_2$Et][Cl]$_2$ and [$^{Mes}$NHC$_2$Et][Cl]$_2$ have been used as precursors for dipalladium complexes for Heck reactions (Li *et al.*, 2013; Yang *et al.*, 2012; Cao *et al.*, 2010), while [$^{tBu}$NHC$_2$Et][Br]$_2$ was a precursor for dimetallic Rh complexes (Wells *et al.*, 2008) and mixed-metal Rh/Pd (Zamora *et al.*, 2009) and Ir/Rh (Frey *et al.*, 2006). Similarly, [$^{Mes}$NHC$_2$Me][Br]$_2$ and [$^{Mes}$NHC$_2$Et][Br]$_2$ were used to synthesize bimetallic gold catalysts for cross-coupling and hydroamination reactions (Baron *et al.*, 2018).




**[$^{tBu}$NHC$_2$Me][Br]$_2$** R = *tert*-butyl; R$^1$ = CH$_2$, n = 1

**[$^{tBu}$NHC$_2$Et][Br]$_2$** R = *tert*-butyl; R$^1$ = CH$_2$CH$_2$, n = 2

**[$^{Mes}$NHC$_2$Me][Br]$_2$** R = 2,4,6-trimethylphenyl; R$^1$ = CH$_2$, n = 2

**[$^{Mes}$NHC$_2$Et][Br]$_2$** R = 2,4,6-trimethylphenyl; R$^1$ = CH$_2$CH$_2$, n = 4

While bis(imidazolium) salts are common ligand precursors, few have been structurally characterized (Rheingold, 2019). This work presents structural characterization and a comparison of supramolecular features for methylene- *versus* ethylene-linked bis(imidazolium) salts with *tert*-butyl and mesityl ancillary groups.

## 2. Structural commentary

All four bis(imidazolium) salts were recrystallized from hot methanol and each compound co-crystallizes with one or more molecules of water. Fig. 1 depicts [$^{tBu}$NHC$_2$Me][Br]$_2$·H$_2$O while Fig. 2 depicts [$^{tBu}$NHC$_2$Et][Br]$_2$·2H$_2$O.

Bond distances in the imidazolium rings of [$^{tBu}$NHC$_2$Me][Br]$_2$·H$_2$O and [$^{tBu}$NHC$_2$Et][Br]$_2$·2H$_2$O are mostly the same within experimental error, with backbone C2—C3 distances of 1.348 (4) and 1.349 (3) Å, respectively. The N—C distances are also mostly comparable with [$^{tBu}$NHC$_2$Me][Br]$_2$·H$_2$O having an N1—C2 and an N2—C3 distance of 1.389 (3) Å and N1—C1 and N2—C1 distances both being 1.337 (3) Å, while [$^{tBu}$NHC$_2$Et][Br]$_2$·2H$_2$O has an N1—C2 distance of 1.388 (3) Å, an N2—C3 distance of 1.384 (3) Å, an

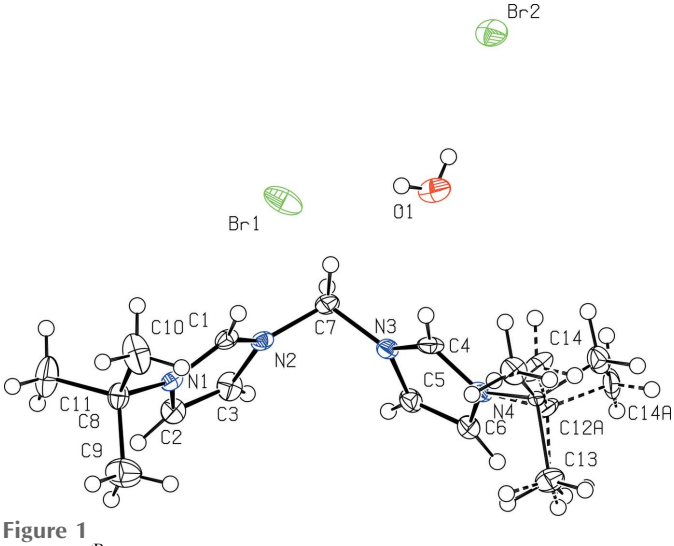



**Figure 1**
View of [$^{tBu}$NHC$_2$Me][Br]$_2$·H$_2$O with 50% probability ellipsoids.

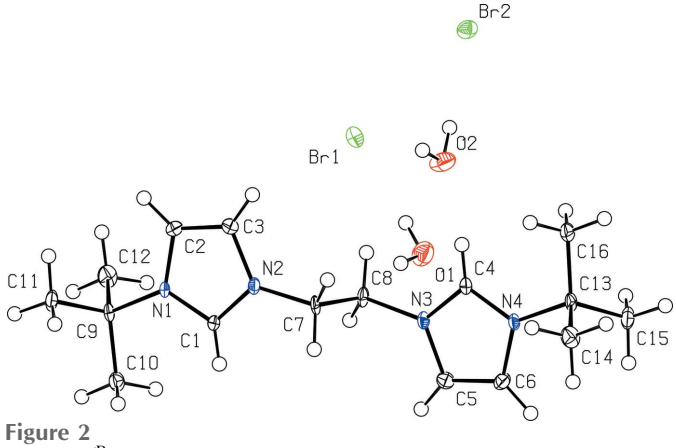



**Figure 2**
View of [$^{tBu}$NHC$_2$Et][Br]$_2$·2H$_2$O with 50% probability ellipsoids.

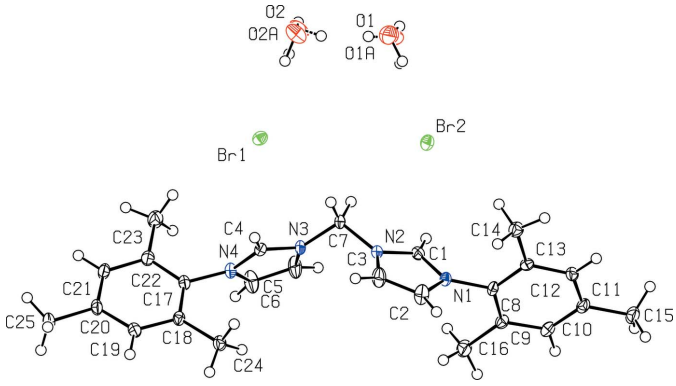



**Figure 3**
View of $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$ with 50% probability ellipsoids.

N1—C1 distance of 1.327 (3) Å and an N2—C1 distance of 1.331 (3) Å. For the linker, the N2—C7 distance is 1.463 (3) Å for $[^{tBu}NHC_2Me][Br]_2{\cdot}H_2O$ and 1.468 (3) Å for $[^{tBu}NHNHC_2Et][Br]_2{\cdot}2H_2O$.

Bond angles in the imidazolium rings are also quite similar in $[^{tBu}NHC_2Me][Br]_2{\cdot}H_2O$ and $[^{tBu}NHC_2Et][Br]_2{\cdot}2H_2O$. For $[^{tBu}NHC_2Me][Br]_2{\cdot}H_2O$, bond angles include C1—N1—C2 at 108.2 (2)°, N1—C2—C3 at 107.6 (2)°, C2—C3—N2 at 106.9 (2)°, C3—N2—C1 at 108.6 (2)°, and N2—C1—N1 at 108.7 (2)°. For $[^{tBu}NHC_2Et][Br]_2{\cdot}H_2O$, bond angles include C1—N1—C2 at 108.21 (19)°, N1—C2—C3 at 107.3 (2)°, C2—C3—N2 at 106.9 (2)°, C3—N2—C1 at 108.54 (19)°, and N2—C1—N1 at 109.02 (19)°.

Fig. 3 depicts $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$ while Fig. 4 depicts $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$. Notably, $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$ is the only compound of the four for which the asymmetric unit contains only half of the molecule.

Bond distances in the imidazolium rings of $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$ and $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$ are mostly the same within experimental error, with backbone C2—C3 distances of 1.344 (3) and 1.3506 (19) Å, respectively. N—C distances are also mostly the same with $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$ having an N1—C2 distance of 1.387 (3) Å, an N2—C3 distance of 1.380 (3) Å, an N1—C1 distance of 1.326 (3) Å, and an N2—C1 distance of 1.341 (3) Å. Similarly, $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$ has an N1—C2 distance of 1.3872 (16) Å, an N2—C3 distance of 1.3841 (16) Å, an N1—C1 distance of 1.3322 (16) Å and an N2—C1 distance of 1.3314 (16) Å. For the linker, the N2—C7 distance is 1.457 (3) Å for $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$ and 1.4653 (16) Å for $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$.

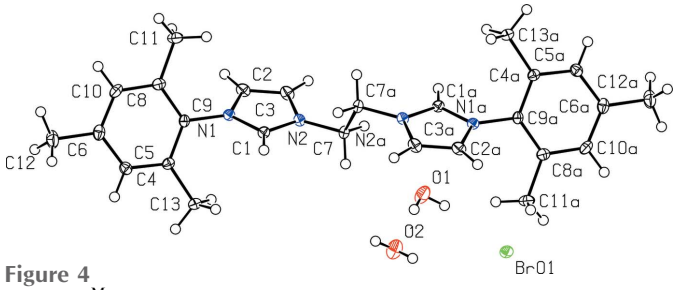



**Figure 4**
View of $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$ with 50% probability ellipsoids.

Bond angles in the imidazolium rings are also mostly the same for $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$ and $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$. For $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$, bond angles include C1—N1—C2 at 108.92 (17)°, N1—C2—C3 at 107.20 (19)°, C2—C3—N2 at 106.95 (19)°, C3—N2—C1 at 108.96 (17)°, and N2—C1—N1 at 107.96 (18)°. For $[^{Mes}NHC_2Et][Br]_2{\cdot}4H_2O$, bond angles include C1—N1—C2 at 108.51 (11)°, N1—C2—C3 at 107.19 (11)°, C2—C3—N2 at 106.87 (11)°, C3—N2—C1 at 108.89 (11)°, and N2—C1—N1 at 108.54 (11)°. Overall, these data support that changing the linker $R^1$ group from methylene to ethylene does not significantly affect the imidazolium ring structures.

## 3. Supramolecular features

The supramolecular structure of $[^{tBu}NHC_2Me][Br]_2{\cdot}H_2O$ is stabilized by hydrogen bonding (Fig. 5, Table 1). Distances between centroids of neighboring imidazoles are greater than 5 Å, suggesting no $\pi$-stacking interactions (Janiak, 2000). Hydrogen bonding between one bromide atom and one water molecule is found with Br1···H1*D* having a distance of 2.575 (4) Å. One *tert*-butyl group has positional disorder.

The supramolecular structure of $[^{tBu}NHC_2Et][Br]_2{\cdot}2H_2O$ is stabilized by extensive hydrogen bonding (Fig. 6, Table 1). Distances between centroids of neighboring imidazoles are greater than 5 Å, suggesting no $\pi$-stacking interactions (Janiak, 2000). Several hydrogen-bonding interactions are found between bromide ions and water molecules, including Br2···H1*B* (2.439 Å) and Br1···H1*A* (2.398 Å).

The supramolecular structure of $[^{Mes}NHC_2Me][Br]_2{\cdot}2H_2O$ is also stabilized by hydrogen bonding (Fig. 7, Table 1). No $\pi$-stacking interactions were found as distances between

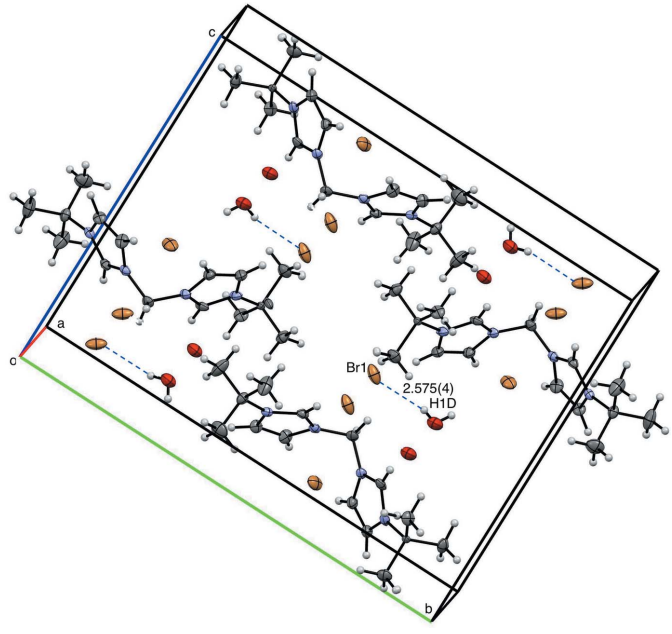



**Figure 5**
View of four molecules of $[^{tBu}NHC_2Me][Br]_2{\cdot}H_2O$ with 50% probability ellipsoids, highlighting intermolecular distances. Disordered *tert*-butyl groups are omitted for clarity.

**Table 1**
Intermolecular distances (Å) in the unit cells of $[^{R}NHC_2R_1][X]_2{\cdot}nH_2O$.

Standard deviations for distances including some H atoms are omitted where H atoms were positionally fixed.

| Compound | Atoms | Distance |
|---|---|---|
| $[^{t\mathrm{Bu}}NHC_2Me][Br]_2{\cdot}H_2O$ | Br1···H1*D* | 2.575 (4) |
| $[^{t\mathrm{Bu}}NHC_2Et][Br]_2{\cdot}2H_2O$ | Br1···H1*A* | 2.398 |
| | Br2···H1*B* | 2.439 |
| $[^{\mathrm{Mes}}NHC_2Me][Br]_2{\cdot}2H_2O$ | Br1···H2*A* | 2.413 |
| | Br2···H1*A* | 2.463 |
| | O1*A*···H2*B* | 2.125 |
| $[^{\mathrm{Mes}}NHC_2Et][Br]_2{\cdot}4H_2O$ | O1···H2*B* | 1.994 (2) |
| | O2···H1*E* | 2.001 (3) |
| | Br1···H1*D* | 2.585 (2) |

centroids of aromatic rings of neighboring molecules are greater than 5 Å (Janiak, 2000). Several hydrogen-bonding interactions are observed between bromide ions and water molecules as well as neighboring water molecules, including Br1···H2*A* at 2.413 Å, Br2···H1*A* at 2.463 Å, and O1*A*···H2*B* at 2.125 Å.

The supramolecular structure of $[^{\mathrm{Mes}}NHC_2Et][Br]_2{\cdot}4H_2O$ is also stabilized by hydrogen bonding (Fig. 8, Table 1). No $\pi$-stacking is observed between mesityl groups, similar to $[^{\mathrm{Mes}}NHC_2Me][Br]_2{\cdot}2H_2O$ as the distance between centroids of the mesityl groups of neighboring fragments is greater than 4.5 Å (Janiak, 2000). Hydrogen-bonding interactions include O1···H2*B* at 1.994 (2) Å, O2···H1*E* at 2.001 (3) Å, and Br1···H1*D* at 2.585 (2) Å.

## 4. Database survey

A survey of the Cambridge Structural Database (Web accessed March 24, 2022; Groom *et al.*, 2016) and SciFinder (SciFinder, 2022) yielded no exact matches for the unit cells of $[^{t\mathrm{Bu}}NHC_2Me][Br]_2{\cdot}H_2O$, $[^{t\mathrm{Bu}}NHC_2Et][Br]_2{\cdot}2H_2O$, or $[^{\mathrm{Mes}}NHC_2Et][Br]_2{\cdot}4H_2O$. A deposited dataset for $[^{\mathrm{Mes}}NHC_2Me][Br]_2{\cdot}2H_2O$ was found (Rheingold, 2019) with a slightly higher *R*1 of 3.94% and data collection at a higher temperature of 150 K, as compared to *R*1 of 3.18% and temperature of 112 K in the current report. As discussed in the introduction, the syntheses of all of the reported structures are reported based on the SciFinder search; however, no additional structural data were found.

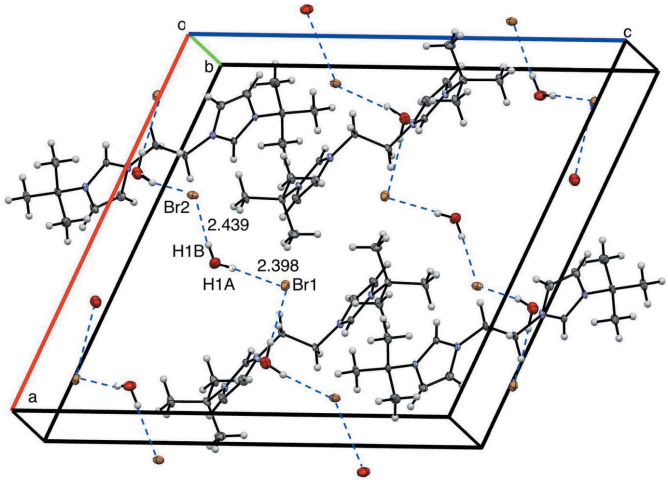



**Figure 6**
View of four molecules of $[^{t\mathrm{Bu}}NHC_2Et][Br]_2{\cdot}2H_2O$ with 50% probability ellipsoids, highlighting intermolecular distances.

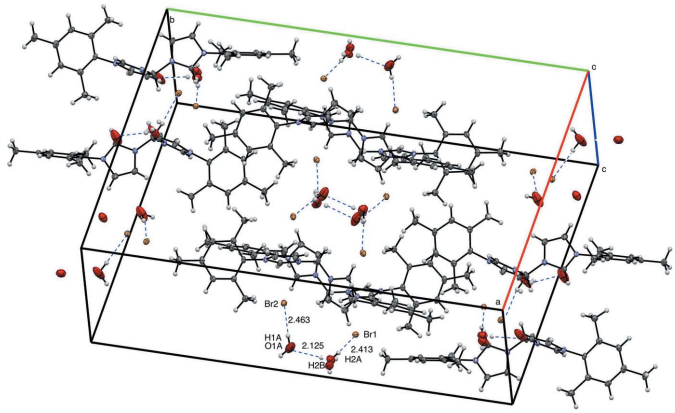



**Figure 7**
View of eight molecules of $[^{\mathrm{Mes}}NHC_2Me][Br]_2{\cdot}2H_2O$ with 50% probability ellipsoids, highlighting intermolecular distances.

## 5. Synthesis and crystallization

**General considerations.** All reagents were purchased from commercial suppliers and used without further purification. $^1$H

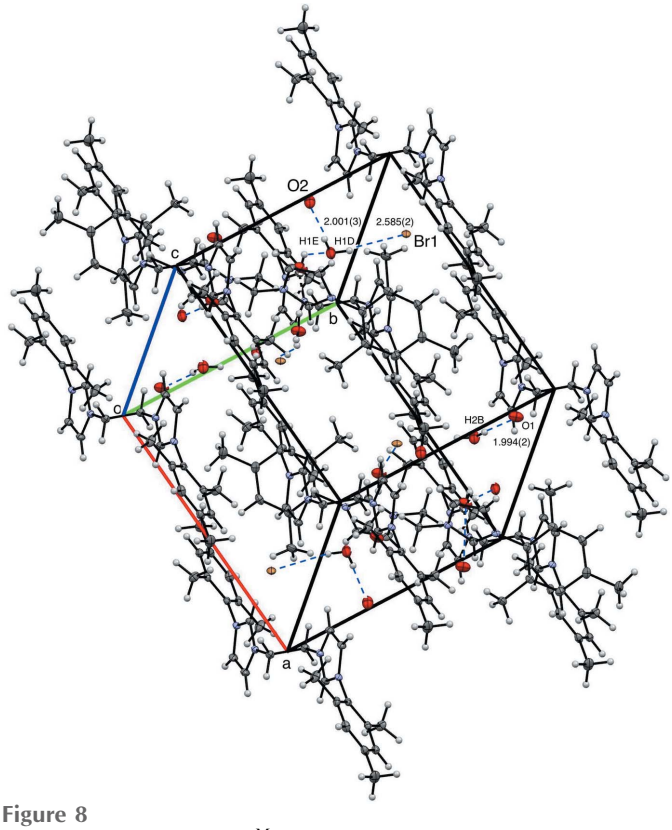



**Figure 8**
View of eight molecules of $[^{\mathrm{Mes}}NHC_2Et][Br]_2{\cdot}4H_2O$ with 50% probability ellipsoids, highlighting intermolecular distances.

NMR data were collected on a Varian 400 MHz spectrometer and referenced to residual $CHCl_3$.

**Synthesis of 1-*tert*-butyl-1*H*-imidazole, ($^{tBu}$Im).** The procedure was adapted from a literature procedure (Liu *et al.*, 2003). A round-bottom flask was charged with 10.0 mL (95 mmol, 1 eq.) of *tert*-butylamine, 11.0 mL of 40% glyoxal (95 mmol, 1 eq.), approximately 100 mL of methanol, and approximately 25 mL of deionized water and a stir bar, then heated to 343 K under reflux. 7.81 mL of 37% formaldehyde (95 mmol, 1 eq.) were added, followed by 3.70 mL of ammonium hydroxide (95 mmol, 1 eq.) added dropwise over 5 minutes while stirring. The solution was refluxed at 343 K for 5 h, resulting in a light red–orange solution. Excess solvent was removed *in vacuo*, and the resulting product was diluted with approximately 150 mL of dichloromethane and washed twice with 50 mL of deionized $H_2O$ until the aqueous layers ran clear. The product was vacuum distilled at ∼373 K, yielding a clear liquid, which was weighed in a tared vial, resulting in 7.95 g (34% yield) of $^{tBu}$Im, and characterized by $^1$H NMR spectroscopy in $CDCl_3$.

**Synthesis of 1-(2,4,6-trimethylphenyl)-1*H*-imidazole, ($^{Mes}$Im).** The procedure was adapted from a literature procedure (Liu *et al.*, 2003; Gardiner *et al.*, 1999). A 250 mL three-neck round-bottom flask was charged with 15.000 g (110.9 mmol, 1 eq.) of 2,4,6-trimethylaniline, 16.090 g (110.9 mmol, 1 eq) of 40% glyoxal, and ∼75 mL of methanol and stirred for 24 h after which the solution turned orange with a yellow precipitate. 11.86 g (221.8 mmol, 2 eq.) of ammonium chloride, 18.00 g (221.8 mmol, 2 eq.) of 37% formaldehyde, and 300 mL of methanol were added, and the solution was refluxed for 24 h at 373 K, at which point the solution was deep brown. After being cooled to room temperature, 25.57 g (221.8 mmol, 2 eq.) of 85% phosphoric acid were added dropwise over ten minutes and the solution was refluxed for 16 h at 368 K. Excess solvent was removed *in vacuo* at 313 K, and the viscous brown residue was poured over ∼300 g of ice and neutralized to pH 10 with a saturated solution of potassium hydroxide, resulting in a clear solution with a chunky brown precipitate. The product was taken into diethyl ether by washing the solution three times with ∼100 mL of diethyl ether. The diethyl ether solution was washed thrice with ∼100 mL of water, thrice with ∼100 mL of brine, and dried overnight over sodium sulfate. Sodium sulfate solids were gravity filtered from the solution and the solvent was removed *in vacuo* resulting in a brown solid. The product was recrystallized from hot ethyl acetate, resulting in 9.49 g (46% yield) of tan crystals, which were characterized by $^1$H NMR spectroscopy and identified as $^{Mes}$Im.

**Synthesis of 1,1′-di(*tert*-butyl)-3,3′-methylene-diimidazolium dibromide, [$^{tBu}$NHC$_2$Me][Br]$_2$.** 1.850 g (14.9 mmol, 2.5 eq.) of $^{tbu}$Im and 0.4194 mL (5.9 mmol, 1 eq.) of dibromomethane, a stir bar, and ∼20 mL of toluene were stirred in a 50 mL round-bottomed flask. The solution was then heated to 423 K and refluxed for 46 h, resulting in the formation of a dark orange–brown solution. The solution was cooled in an ice bath, resulting in a fine white precipitate which was collected *via* vacuum filtration, washed twice with ∼5 mL of cold toluene, filtered and dried. 1.120 g (78.02% yield) of a fine white solid identified as [$^{tBu}$NHC$_2$Me][Br]$_2$ were isolated. Crystals suitable for X-ray diffraction were obtained by recrystallization from hot methanol. The product was characterized by $^1$H NMR spectroscopy. The $^1$H NMR data were consistent with those previously reported (Scherg *et al.*, 2006).

**Synthesis of 1,1′-di(*tert*-butyl)-3,3′-ethylene-diimidazolium dibromide [$^{tBu}$NHC$_2$Et][Br]$_2$.** A 250 mL round-bottomed flask was charged with 2.017 g (16.2 mmol, 2.5 eq.) of $^{tbu}$Im, 0.562 mL (6.45 mmol, 1 eq.) of dibromoethane, a stir bar, and ∼20 mL of toluene. The mixture was refluxed at 423 K and stirred for 46 h, at which point the solution was a rusty brown color. The flask was then placed in an ice bath, and the resulting precipitate was collected *via* vacuum filtration and washed twice with ∼5 mL of cold toluene. The resulting solids were dried and weighed, yielding 1.727 g (61% yield) of [$^{tBu}$NHC$_2$Et][Br]$_2$ and single crystals suitable for X-ray diffraction were obtained *via* recrystallization from hot methanol. $^1$H NMR data were consistent with those previously reported (Scherg *et al.*, 2006).

**Synthesis of 1,1′-di(mesityl)-3,3′-methylene-diimidazolium dibromide, [$^{Mes}$NHC$_2$Me][Br]$_2$.** The procedure was adapted from a literature procedure (Gardiner *et al.*, 1999). 5.00 g (26.8 mmol, 2.5 eq.) of $^{Mes}$Im we added to a 50 mL round-bottomed flask with a stir bar and ∼20 mL of toluene. 0.754 mL (10.72 mmol, 1 eq.) of dibromomethane were added and the solution was refluxed at 423 K for 20 h. The solution was cooled in an ice bath, resulting in a white precipitate. The white solid was recrystallized from ∼12 mL of hot methanol. The product was obtained in 17% yield (1.10 g) as tan crystals identified as [$^{Mes}$NHC$_2$Me][Br]$_2$ suitable for X-ray diffraction and characterized by $^1$H NMR.

**Synthesis of 1,1′-di(mesityl)-3,3′-ethylene-diimidazolium dibromide, [$^{Mes}$NHC$_2$Et][Br]$_2$.** A 250 mL three-neck round-bottom flask was charged with 4.438 g (23.8 mmol, 2.5 eq.) of $^{Mes}$Im, 0.824 mL (9.52 mmol, 1 eq.) of 1,2-dibromoethane, and ∼20 mL of toluene. The reaction mixture was heated to 423 K and refluxed for 19 h, resulting in a cloudy yellow solution. The solution was cooled in an ice bath and the precipitate was collected and recrystallized from ∼25 mL of hot methanol, resulting in 2.962 g (55% yield) of tan crystals which were analyzed *via* $^1$H NMR spectroscopy and identified as [$^{Mes}$NHC$_2$Et][Br]$_2$.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Most hydrogen atoms were placed in calculated positions using the AFIX commands of *SHELXL* and included as riding contributions with distances of 0.95 Å for C—H, 0.99 Å for $CH_2$ and 0.98 Å for $CH_3$. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}$ values of riding H atoms were set to 1.2 times $U_{eq}$(C) for CH and $CH_2$, and 1.5 times $U_{eq}$(C) for $CH_3$ and $H_2O$. For [$^{tBu}$NHC$_2$Me][Br]$_2$, the SADI command of *SHELX* was used to model disorder in one of the *tert*-butyl moieties for N4—C0*AA* and N4—C12,

**Table 2**
Experimental details.

| | [$^{Mes}$NHC$_2$Me][Br]$_2$·2H$_2$O | [$^{tBu}$NHC$_2$Me][Br]$_2$·H$_2$O | [$^{tBu}$NHC$_2$Et][Br]$_2$·2H$_2$O | [$^{Mes}$NHC$_2$Et][Br]$_2$·4H$_2$O |
|---|---|---|---|---|
| Crystal data | | | | |
| Chemical formula | $C_{25}H_{30}N_4^{2+}$·2Br$^-$·2H$_2$O | $C_{15}H_{26}N_4^{+}$·2Br$^-$·H$_2$O | $C_{16}H_{28}N_4^{2+}$·2Br$^-$·2H$_2$O | $C_{26}H_{32}N_4^{2+}$·2Br$^-$·4H$_2$O |
| $M_r$ | 582.38 | 440.23 | 472.27 | 632.42 |
| Crystal system, space group | Orthorhombic, *Pccn* | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/c$ |
| Temperature (K) | 112 | 293 | 100 | 100 |
| $a$, $b$, $c$ (Å) | 21.5695 (6), 28.3385 (6), 8.9401 (2) | 7.211 (5), 18.311 (17), 15.409 (5) | 17.1577 (6), 7.3180 (2), 18.2712 (6) | 12.4230 (3), 13.1447 (3), 9.2780 (2) |
| $\alpha$, $\beta$, $\gamma$ (°) | 90, 90, 90 | 90, 101.35 (3), 90 | 90, 112.786 (1), 90 | 90, 108.379 (1), 90 |
| $V$ (Å$^3$) | 5464.6 (2) | 1995 (2) | 2115.09 (12) | 1437.78 (6) |
| $Z$ | 8 | 4 | 4 | 2 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 2.99 | 4.07 | 3.85 | 2.86 |
| Crystal size (mm) | 0.4 × 0.3 × 0.25 | 0.3 × 0.15 × 0.1 | 0.2 × 0.1 × 0.05 | 0.15 × 0.15 × 0.05 |
| Data collection | | | | |
| Diffractometer | Bruker Venture D8 Kappa | Bruker APEXII CCD | Bruker Venture D8 Kappa | Bruker Venture D8 Kappa |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2016) | Multi-scan (*SADABS*; Bruker, 2016) | Multi-scan (*SADABS*; Bruker, 2016) | Multi-scan (*SADABS*; Bruker, 2016) |
| $T_{min}$, $T_{max}$ | 0.386, 0.748 | 0.544, 0.747 | 0.496, 0.748 | 0.544, 0.750 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 39085, 5954, 5530 | 33565, 4402, 3780 | 31474, 4664, 4168 | 28199, 3165, 3028 |
| $R_{int}$ | 0.035 | 0.043 | 0.059 | 0.025 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.641 | 0.641 | 0.641 | 0.641 |
| Refinement | | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.032, 0.066, 1.19 | 0.035, 0.068, 1.08 | 0.031, 0.066, 1.11 | 0.018, 0.044, 1.10 |
| No. of reflections | 5954 | 4402 | 4664 | 3165 |
| No. of parameters | 338 | 259 | 253 | 194 |
| No. of restraints | 0 | 3 | 0 | 0 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.42, −0.54 | 1.49, −1.10 | 0.60, −0.61 | 0.33, −0.29 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

C0*AA*—C00*N* and C14—C12, and C1*AA*—C0*AA* and C13—C12 to restrain distances within a sigma of 0.02 Å. The population parameters for the disordered *tert*-butyl groups are 0.54019 for C12–C14, and 0.45981 for C00*N*, C0*AA*, and C1*AA*. The highest peak and deepest hole are both near a heavy atom Br1 with a distance of 0.88 Å from the highest peak of 1.49 e Å$^{-3}$ and a distance of 0.73 Å from the deepest hole of −1.10 e Å$^{-3}$.

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# supporting information

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## Effect of methylene *versus* ethylene linkers on structural properties of *tert*-butyl and mesityl bis(imidazolium) bromide salts

**Emily S. Thompson, Elisa M. Olivas, Adrian Torres, Briana C. Arreaga, Hector L. Alarcon, Deandrea Dolberry, Jacob P. Brannon and S. Chantal E. Stieber**

### Computing details

For all structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016). Program(s) used to solve structure: SHELXT (Sheldrick, 2015a) for sces01006_0m, est01043_0m, est01041d_0ma; *olex2.solve* (Bourhis *et al.*, 2015) for at01019_0ma. For all structures, program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### 1,1′-Methylenebis(3-*tert*-butylimidazolium) dibromide monohydrate (sces01006_0m)

*Crystal data*

$C_{15}H_{26}N_4^+ \cdot 2Br^- \cdot H_2O$
$M_r$ = 440.23
Monoclinic, $P2_1/c$
$a$ = 7.211 (5) Å
$b$ = 18.311 (17) Å
$c$ = 15.409 (5) Å
$\beta$ = 101.35 (3)°
$V$ = 1995 (2) Å$^3$
$Z$ = 4
$F(000)$ = 896
$D_x$ = 1.466 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9889 reflections
$\theta$ = 2.6–30.2°
$\mu$ = 4.07 mm$^{-1}$
$T$ = 293 K
Prism, clear colourless
0.3 × 0.15 × 0.1 mm

*Data collection*

Bruker APEXII CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.544, $T_{max}$ = 0.747
33565 measured reflections
4402 independent reflections
3780 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043
$\theta_{max}$ = 27.1°, $\theta_{min}$ = 2.7°
$h$ = −9→8
$k$ = −23→23
$l$ = −19→19

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.068
$S$ = 1.08
4402 reflections
259 parameters
3 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0006P)^2 + 4.1194P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.49 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.10 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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Br2 | 0.83773 (4) | 0.86331 (2) | 0.55378 (2) | 0.03323 (9) | |
| Br1 | 1.05299 (4) | 0.61882 (2) | 0.35706 (2) | 0.03727 (10) | |
| N3 | 0.4514 (3) | 0.71177 (11) | 0.18236 (13) | 0.0175 (4) | |
| N1 | 0.5823 (3) | 0.48054 (11) | 0.16964 (13) | 0.0162 (4) | |
| O1 | 0.8362 (4) | 0.78047 (16) | 0.35775 (17) | 0.0419 (6) | |
| N2 | 0.4742 (3) | 0.58205 (11) | 0.21324 (13) | 0.0170 (4) | |
| N4 | 0.5288 (3) | 0.80162 (12) | 0.10500 (14) | 0.0225 (5) | |
| C1 | 0.6311 (4) | 0.54357 (13) | 0.21172 (16) | 0.0181 (5) | |
| H5 | 0.753852 | 0.558228 | 0.235943 | 0.022* | |
| C5 | 0.2905 (4) | 0.73014 (14) | 0.12095 (18) | 0.0221 (5) | |
| C4 | 0.5935 (4) | 0.75572 (14) | 0.17061 (16) | 0.0211 (5) | |
| H9 | 0.716674 | 0.754245 | 0.203041 | 0.025* | |
| C7 | 0.4681 (4) | 0.65531 (14) | 0.25048 (16) | 0.0212 (5) | |
| H8A | 0.361201 | 0.658686 | 0.279890 | 0.025* | |
| H8B | 0.582372 | 0.663573 | 0.294434 | 0.025* | |
| C8 | 0.7152 (4) | 0.42139 (14) | 0.15085 (18) | 0.0207 (5) | |
| C6 | 0.3396 (4) | 0.78602 (15) | 0.07277 (19) | 0.0251 (6) | |
| C2 | 0.3869 (4) | 0.47957 (15) | 0.14242 (18) | 0.0216 (5) | |
| C3 | 0.3195 (4) | 0.54263 (15) | 0.16910 (19) | 0.0239 (6) | |
| C13 | 0.5981 (4) | 0.86039 (16) | −0.02694 (18) | 0.0290 (6) | |
| H15A | 0.613085 | 0.812884 | −0.050991 | 0.043* | 0.54 (3) |
| H15B | 0.674562 | 0.895007 | −0.050884 | 0.043* | 0.54 (3) |
| H15C | 0.467761 | 0.874789 | −0.042171 | 0.043* | 0.54 (3) |
| H15D | 0.641328 | 0.812747 | −0.039773 | 0.043* | 0.46 (3) |
| H15E | 0.674290 | 0.896891 | −0.047847 | 0.043* | 0.46 (3) |
| H15F | 0.468475 | 0.866370 | −0.055952 | 0.043* | 0.46 (3) |
| C12 | 0.6629 (17) | 0.8579 (5) | 0.0781 (8) | 0.014 (2) | 0.54 (3) |
| C11 | 0.6634 (5) | 0.35011 (16) | 0.1920 (2) | 0.0402 (8) | |
| H3A | 0.676730 | 0.356294 | 0.254815 | 0.060* | |
| H3B | 0.746068 | 0.311841 | 0.180278 | 0.060* | |
| H3C | 0.534897 | 0.337462 | 0.166825 | 0.060* | |
| C10 | 0.9155 (4) | 0.44460 (17) | 0.1903 (3) | 0.0408 (8) | |
| H1A | 0.944282 | 0.489150 | 0.162880 | 0.061* | |
| H1B | 1.002017 | 0.407121 | 0.180300 | 0.061* | |
| H1C | 0.927348 | 0.452256 | 0.252799 | 0.061* | |
| C9 | 0.6908 (5) | 0.4157 (2) | 0.0510 (2) | 0.0399 (8) | |
| H4A | 0.564299 | 0.400122 | 0.026305 | 0.060* | |

| | | | | | |
|---|---|---|---|---|---|
| H4B | 0.779299 | 0.380851 | 0.036360 | 0.060* | |
| H4C | 0.713383 | 0.462547 | 0.027048 | 0.060* | |
| C15 | 0.8712 (15) | 0.8362 (6) | 0.1050 (8) | 0.0245 (19) | 0.54 (3) |
| H13A | 0.906281 | 0.834192 | 0.168381 | 0.037* | 0.54 (3) |
| H13B | 0.948184 | 0.871611 | 0.082775 | 0.037* | 0.54 (3) |
| H13C | 0.889802 | 0.789067 | 0.080737 | 0.037* | 0.54 (3) |
| C14 | 0.6197 (18) | 0.9291 (5) | 0.1206 (7) | 0.025 (2) | 0.54 (3) |
| H14A | 0.487306 | 0.939908 | 0.103235 | 0.038* | 0.54 (3) |
| H14B | 0.692055 | 0.967891 | 0.101603 | 0.038* | 0.54 (3) |
| H14C | 0.652454 | 0.924641 | 0.183859 | 0.038* | 0.54 (3) |
| H1D | 0.905 (6) | 0.746 (2) | 0.365 (3) | 0.061 (15)* | |
| C14A | 0.530 (3) | 0.9398 (5) | 0.0928 (10) | 0.034 (3) | 0.46 (3) |
| H00A | 0.398530 | 0.942603 | 0.064831 | 0.050* | 0.46 (3) |
| H00B | 0.596718 | 0.980230 | 0.074007 | 0.050* | 0.46 (3) |
| H00C | 0.540922 | 0.941501 | 0.155917 | 0.050* | 0.46 (3) |
| C12A | 0.614 (2) | 0.8681 (6) | 0.0668 (11) | 0.021 (3) | 0.46 (3) |
| C15A | 0.823 (2) | 0.8614 (11) | 0.1096 (10) | 0.038 (3) | 0.46 (3) |
| H1AA | 0.837624 | 0.866529 | 0.172622 | 0.057* | 0.46 (3) |
| H1AB | 0.893103 | 0.898947 | 0.087072 | 0.057* | 0.46 (3) |
| H1AC | 0.868755 | 0.814380 | 0.096076 | 0.057* | 0.46 (3) |
| H1E | 0.839 (5) | 0.800 (2) | 0.399 (3) | 0.041 (12)* | |
| H6 | 0.331 (4) | 0.4388 (16) | 0.1108 (19) | 0.023 (7)* | |
| H11 | 0.270 (5) | 0.8115 (18) | 0.027 (2) | 0.035 (9)* | |
| H10 | 0.175 (5) | 0.7062 (18) | 0.118 (2) | 0.037 (9)* | |
| H7 | 0.201 (5) | 0.5612 (17) | 0.164 (2) | 0.034 (9)* | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br2 | 0.02663 (15) | 0.03928 (17) | 0.02985 (16) | 0.01469 (13) | −0.00401 (11) | −0.00144 (13) |
| Br1 | 0.02382 (15) | 0.0520 (2) | 0.03702 (18) | −0.01154 (13) | 0.00837 (12) | −0.02086 (14) |
| N3 | 0.0203 (11) | 0.0185 (10) | 0.0146 (10) | −0.0049 (8) | 0.0058 (8) | −0.0011 (8) |
| N1 | 0.0134 (10) | 0.0203 (11) | 0.0140 (10) | −0.0024 (8) | 0.0008 (8) | 0.0046 (8) |
| O1 | 0.0559 (17) | 0.0417 (15) | 0.0233 (13) | −0.0041 (13) | −0.0040 (11) | 0.0034 (11) |
| N2 | 0.0182 (11) | 0.0207 (11) | 0.0125 (10) | −0.0039 (8) | 0.0040 (8) | 0.0026 (8) |
| N4 | 0.0315 (13) | 0.0209 (11) | 0.0153 (11) | −0.0117 (9) | 0.0053 (9) | −0.0034 (8) |
| C1 | 0.0149 (12) | 0.0223 (13) | 0.0156 (12) | −0.0039 (10) | −0.0009 (9) | 0.0041 (10) |
| C5 | 0.0210 (14) | 0.0194 (13) | 0.0241 (14) | −0.0026 (10) | 0.0002 (11) | −0.0025 (10) |
| C4 | 0.0243 (14) | 0.0283 (14) | 0.0106 (12) | −0.0092 (11) | 0.0035 (10) | −0.0022 (10) |
| C7 | 0.0285 (14) | 0.0233 (13) | 0.0135 (12) | −0.0036 (11) | 0.0083 (10) | 0.0014 (10) |
| C8 | 0.0176 (13) | 0.0180 (12) | 0.0271 (14) | −0.0015 (10) | 0.0060 (11) | 0.0024 (10) |
| C6 | 0.0304 (15) | 0.0196 (13) | 0.0227 (14) | −0.0033 (11) | −0.0010 (12) | −0.0013 (11) |
| C2 | 0.0126 (12) | 0.0246 (14) | 0.0266 (14) | −0.0068 (10) | 0.0016 (10) | 0.0013 (11) |
| C3 | 0.0136 (13) | 0.0256 (14) | 0.0328 (16) | −0.0051 (11) | 0.0053 (11) | 0.0022 (11) |
| C13 | 0.0353 (16) | 0.0344 (16) | 0.0195 (14) | −0.0012 (13) | 0.0109 (12) | 0.0030 (12) |
| C12 | 0.023 (5) | 0.011 (3) | 0.008 (4) | −0.003 (3) | 0.002 (4) | 0.000 (3) |
| C11 | 0.0429 (19) | 0.0235 (15) | 0.060 (2) | 0.0033 (13) | 0.0254 (17) | 0.0115 (14) |
| C10 | 0.0166 (15) | 0.0285 (16) | 0.072 (2) | 0.0027 (12) | −0.0039 (15) | −0.0055 (16) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C9 | 0.0406 (19) | 0.050 (2) | 0.0316 (17) | 0.0052 (15) | 0.0133 (14) | −0.0072 (15) |
| C15 | 0.014 (4) | 0.028 (5) | 0.031 (3) | −0.009 (3) | 0.003 (3) | 0.000 (3) |
| C14 | 0.032 (5) | 0.020 (3) | 0.028 (4) | −0.006 (3) | 0.014 (3) | −0.002 (3) |
| C14A | 0.066 (9) | 0.011 (3) | 0.030 (5) | −0.003 (4) | 0.026 (6) | 0.000 (3) |
| C12A | 0.025 (6) | 0.022 (5) | 0.014 (4) | −0.005 (4) | −0.004 (4) | 0.008 (3) |
| C15A | 0.028 (6) | 0.047 (8) | 0.032 (5) | −0.018 (5) | −0.010 (5) | 0.022 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N3—C5 | 1.387 (3) | C13—H15D | 0.9600 |
| N3—C4 | 1.343 (3) | C13—H15E | 0.9600 |
| N3—C7 | 1.461 (3) | C13—H15F | 0.9600 |
| N1—C1 | 1.337 (3) | C13—C12 | 1.595 (13) |
| N1—C8 | 1.512 (3) | C13—C12A | 1.434 (16) |
| N1—C2 | 1.389 (3) | C12—C15 | 1.530 (10) |
| O1—H1D | 0.80 (4) | C12—C14 | 1.519 (10) |
| O1—H1E | 0.73 (4) | C11—H3A | 0.9600 |
| N2—C1 | 1.337 (3) | C11—H3B | 0.9600 |
| N2—C7 | 1.463 (3) | C11—H3C | 0.9600 |
| N2—C3 | 1.389 (3) | C10—H1A | 0.9600 |
| N4—C4 | 1.327 (3) | C10—H1B | 0.9600 |
| N4—C6 | 1.387 (4) | C10—H1C | 0.9600 |
| N4—C12 | 1.525 (9) | C9—H4A | 0.9600 |
| N4—C12A | 1.531 (11) | C9—H4B | 0.9600 |
| C1—H5 | 0.9300 | C9—H4C | 0.9600 |
| C5—C6 | 1.352 (4) | C15—H13A | 0.9600 |
| C5—H10 | 0.94 (3) | C15—H13B | 0.9600 |
| C4—H9 | 0.9300 | C15—H13C | 0.9600 |
| C7—H8A | 0.9700 | C14—H14A | 0.9600 |
| C7—H8B | 0.9700 | C14—H14B | 0.9600 |
| C8—C11 | 1.529 (4) | C14—H14C | 0.9600 |
| C8—C10 | 1.514 (4) | C14A—H00A | 0.9600 |
| C8—C9 | 1.518 (4) | C14A—H00B | 0.9600 |
| C6—H11 | 0.91 (3) | C14A—H00C | 0.9600 |
| C2—C3 | 1.348 (4) | C14A—C12A | 1.531 (12) |
| C2—H6 | 0.94 (3) | C12A—C15A | 1.527 (11) |
| C3—H7 | 0.91 (3) | C15A—H1AA | 0.9600 |
| C13—H15A | 0.9600 | C15A—H1AB | 0.9600 |
| C13—H15B | 0.9600 | C15A—H1AC | 0.9600 |
| C13—H15C | 0.9600 | | |

| | | | |
|---|---|---|---|
| C5—N3—C7 | 127.0 (2) | C12A—C13—H15F | 109.5 |
| C4—N3—C5 | 108.7 (2) | N4—C12—C13 | 102.7 (7) |
| C4—N3—C7 | 124.3 (2) | N4—C12—C15 | 113.1 (8) |
| C1—N1—C8 | 126.5 (2) | C15—C12—C13 | 111.0 (8) |
| C1—N1—C2 | 108.2 (2) | C14—C12—N4 | 105.6 (7) |
| C2—N1—C8 | 125.2 (2) | C14—C12—C13 | 111.6 (6) |
| H1D—O1—H1E | 112 (4) | C14—C12—C15 | 112.4 (7) |

| | | | |
|---|---|---|---|
| C1—N2—C7 | 125.5 (2) | C8—C11—H3A | 109.5 |
| C1—N2—C3 | 108.6 (2) | C8—C11—H3B | 109.5 |
| C3—N2—C7 | 125.8 (2) | C8—C11—H3C | 109.5 |
| C4—N4—C6 | 108.4 (2) | H3A—C11—H3B | 109.5 |
| C4—N4—C12 | 119.2 (6) | H3A—C11—H3C | 109.5 |
| C4—N4—C12A | 133.6 (7) | H3B—C11—H3C | 109.5 |
| C6—N4—C12 | 132.4 (6) | C8—C10—H1A | 109.5 |
| C6—N4—C12A | 117.7 (7) | C8—C10—H1B | 109.5 |
| N1—C1—N2 | 108.7 (2) | C8—C10—H1C | 109.5 |
| N1—C1—H5 | 125.6 | H1A—C10—H1B | 109.5 |
| N2—C1—H5 | 125.6 | H1A—C10—H1C | 109.5 |
| N3—C5—H10 | 123 (2) | H1B—C10—H1C | 109.5 |
| C6—C5—N3 | 106.5 (2) | C8—C9—H4A | 109.5 |
| C6—C5—H10 | 131 (2) | C8—C9—H4B | 109.5 |
| N3—C4—H9 | 125.7 | C8—C9—H4C | 109.5 |
| N4—C4—N3 | 108.6 (2) | H4A—C9—H4B | 109.5 |
| N4—C4—H9 | 125.7 | H4A—C9—H4C | 109.5 |
| N3—C7—N2 | 111.8 (2) | H4B—C9—H4C | 109.5 |
| N3—C7—H8A | 109.3 | C12—C15—H13A | 109.5 |
| N3—C7—H8B | 109.3 | C12—C15—H13B | 109.5 |
| N2—C7—H8A | 109.3 | C12—C15—H13C | 109.5 |
| N2—C7—H8B | 109.3 | H13A—C15—H13B | 109.5 |
| H8A—C7—H8B | 107.9 | H13A—C15—H13C | 109.5 |
| N1—C8—C11 | 108.4 (2) | H13B—C15—H13C | 109.5 |
| N1—C8—C10 | 108.2 (2) | C12—C14—H14A | 109.5 |
| N1—C8—C9 | 107.0 (2) | C12—C14—H14B | 109.5 |
| C10—C8—C11 | 111.4 (3) | C12—C14—H14C | 109.5 |
| C10—C8—C9 | 109.7 (3) | H14A—C14—H14B | 109.5 |
| C9—C8—C11 | 111.9 (3) | H14A—C14—H14C | 109.5 |
| N4—C6—H11 | 122 (2) | H14B—C14—H14C | 109.5 |
| C5—C6—N4 | 107.7 (2) | H00A—C14A—H00B | 109.5 |
| C5—C6—H11 | 131 (2) | H00A—C14A—H00C | 109.5 |
| N1—C2—H6 | 118.1 (18) | H00B—C14A—H00C | 109.5 |
| C3—C2—N1 | 107.6 (2) | C12A—C14A—H00A | 109.5 |
| C3—C2—H6 | 134.3 (18) | C12A—C14A—H00B | 109.5 |
| N2—C3—H7 | 120 (2) | C12A—C14A—H00C | 109.5 |
| C2—C3—N2 | 106.9 (2) | N4—C12A—C14A | 111.9 (9) |
| C2—C3—H7 | 133 (2) | C13—C12A—N4 | 110.5 (9) |
| H15A—C13—H15B | 109.5 | C13—C12A—C14A | 113.1 (8) |
| H15A—C13—H15C | 109.5 | C13—C12A—C15A | 107.5 (10) |
| H15B—C13—H15C | 109.5 | C15A—C12A—N4 | 101.8 (9) |
| H15D—C13—H15E | 109.5 | C15A—C12A—C14A | 111.4 (10) |
| H15D—C13—H15F | 109.5 | C12A—C15A—H1AA | 109.5 |
| H15E—C13—H15F | 109.5 | C12A—C15A—H1AB | 109.5 |
| C12—C13—H15A | 109.5 | C12A—C15A—H1AC | 109.5 |
| C12—C13—H15B | 109.5 | H1AA—C15A—H1AB | 109.5 |
| C12—C13—H15C | 109.5 | H1AA—C15A—H1AC | 109.5 |
| C12A—C13—H15D | 109.5 | H1AB—C15A—H1AC | 109.5 |

| | |
|---|---|
| C12A—C13—H15E | 109.5 |

| | | | |
|---|---|---|---|
| N3—C5—C6—N4 | −0.3 (3) | C7—N2—C1—N1 | −177.6 (2) |
| N1—C2—C3—N2 | −0.4 (3) | C7—N2—C3—C2 | 177.5 (2) |
| C1—N1—C8—C11 | 122.5 (3) | C8—N1—C1—N2 | 178.4 (2) |
| C1—N1—C8—C10 | 1.6 (3) | C8—N1—C2—C3 | −177.9 (2) |
| C1—N1—C8—C9 | −116.6 (3) | C6—N4—C4—N3 | −0.8 (3) |
| C1—N1—C2—C3 | −0.3 (3) | C6—N4—C12—C13 | −36.8 (9) |
| C1—N2—C7—N3 | 97.2 (3) | C6—N4—C12—C15 | −156.5 (6) |
| C1—N2—C3—C2 | 0.9 (3) | C6—N4—C12—C14 | 80.3 (8) |
| C5—N3—C4—N4 | 0.6 (3) | C6—N4—C12A—C13 | −59.5 (11) |
| C5—N3—C7—N2 | 75.7 (3) | C6—N4—C12A—C14A | 67.4 (12) |
| C4—N3—C5—C6 | −0.2 (3) | C6—N4—C12A—C15A | −173.5 (9) |
| C4—N3—C7—N2 | −105.5 (3) | C2—N1—C1—N2 | 0.8 (3) |
| C4—N4—C6—C5 | 0.7 (3) | C2—N1—C8—C11 | −60.3 (3) |
| C4—N4—C12—C13 | 142.2 (5) | C2—N1—C8—C10 | 178.8 (3) |
| C4—N4—C12—C15 | 22.6 (10) | C2—N1—C8—C9 | 60.6 (3) |
| C4—N4—C12—C14 | −100.7 (6) | C3—N2—C1—N1 | −1.0 (3) |
| C4—N4—C12A—C13 | 127.1 (8) | C3—N2—C7—N3 | −78.8 (3) |
| C4—N4—C12A—C14A | −105.9 (8) | C12—N4—C4—N3 | 179.9 (5) |
| C4—N4—C12A—C15A | 13.1 (14) | C12—N4—C6—C5 | 179.8 (6) |
| C7—N3—C5—C6 | 178.7 (2) | C12A—N4—C4—N3 | 173.0 (8) |
| C7—N3—C4—N4 | −178.3 (2) | C12A—N4—C6—C5 | −174.3 (7) |

**1,1′-(Ethane-1,2-diyl)bis(3-*tert*-butylimidazolium) dibromide dihydrate (est01043_0m)**

*Crystal data*

$C_{16}H_{28}N_4^{2+}\cdot 2Br^-\cdot 2H_2O$
$M_r$ = 472.27
Monoclinic, $P2_1/n$
$a$ = 17.1577 (6) Å
$b$ = 7.3180 (2) Å
$c$ = 18.2712 (6) Å
$\beta$ = 112.786 (1)°
$V$ = 2115.09 (12) Å$^3$
$Z$ = 4
$F(000)$ = 968
$D_x$ = 1.483 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9074 reflections
$\theta$ = 2.4–38.4°
$\mu$ = 3.85 mm$^{-1}$
$T$ = 100 K
Prism, clear colourless
0.2 × 0.1 × 0.05 mm

*Data collection*

Bruker Venture D8 Kappa diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.496, $T_{max}$ = 0.748
31474 measured reflections
4664 independent reflections
4168 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.059
$\theta_{max}$ = 27.1°, $\theta_{min}$ = 2.6°
$h$ = −21→21
$k$ = −9→9
$l$ = −23→23

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.066
$S$ = 1.11
4664 reflections
253 parameters
0 restraints

Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 2.745P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å$^{-3}$
$\Delta\rho_{min} = -0.61$ 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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br2 | 0.42021 (2) | 1.06846 (3) | 0.17436 (2) | 0.01794 (7) |
| Br1 | 0.64204 (2) | 1.22356 (3) | 0.46410 (2) | 0.01716 (7) |
| O2 | 0.60635 (11) | 0.9669 (3) | 0.30798 (12) | 0.0253 (4) |
| H2C | 0.612198 | 1.048204 | 0.344458 | 0.038* |
| H2D | 0.556728 | 0.988924 | 0.271398 | 0.038* |
| O1 | 0.84726 (12) | 1.2201 (3) | 0.50226 (12) | 0.0273 (4) |
| H1C | 0.874519 | 1.260282 | 0.550269 | 0.041* |
| H1D | 0.793229 | 1.222132 | 0.491369 | 0.041* |
| N1 | 0.63968 (11) | 0.5405 (3) | 0.63652 (11) | 0.0097 (4) |
| N2 | 0.70265 (12) | 0.7072 (3) | 0.57816 (11) | 0.0111 (4) |
| N3 | 0.79306 (12) | 0.7383 (3) | 0.42286 (12) | 0.0113 (4) |
| N4 | 0.86030 (11) | 0.8912 (2) | 0.36416 (11) | 0.0103 (4) |
| C1 | 0.70549 (14) | 0.5497 (3) | 0.61555 (13) | 0.0100 (4) |
| C9 | 0.61678 (14) | 0.3834 (3) | 0.67751 (14) | 0.0119 (5) |
| C7 | 0.76212 (14) | 0.7620 (3) | 0.54214 (14) | 0.0123 (5) |
| H1A | 0.818644 | 0.709890 | 0.572987 | 0.015* |
| H1B | 0.767285 | 0.896775 | 0.543092 | 0.015* |
| C4 | 0.79441 (14) | 0.8939 (3) | 0.38544 (13) | 0.0108 (4) |
| C3 | 0.63152 (15) | 0.8025 (3) | 0.57441 (15) | 0.0152 (5) |
| C10 | 0.68416 (16) | 0.2364 (3) | 0.69468 (15) | 0.0165 (5) |
| H9A | 0.688285 | 0.198067 | 0.644913 | 0.025* |
| H9B | 0.668875 | 0.131113 | 0.719524 | 0.025* |
| H9C | 0.738750 | 0.285198 | 0.730682 | 0.025* |
| C2 | 0.59238 (15) | 0.6988 (3) | 0.61096 (15) | 0.0154 (5) |
| C8 | 0.73079 (14) | 0.6942 (3) | 0.45708 (14) | 0.0133 (5) |
| H2A | 0.721968 | 0.560336 | 0.455808 | 0.016* |
| H2B | 0.676038 | 0.752701 | 0.425349 | 0.016* |
| C11 | 0.61411 (16) | 0.4549 (3) | 0.75498 (15) | 0.0176 (5) |
| H7A | 0.670172 | 0.500229 | 0.789205 | 0.026* |
| H7B | 0.597527 | 0.355834 | 0.782054 | 0.026* |
| H7C | 0.572921 | 0.554573 | 0.743410 | 0.026* |
| C5 | 0.86096 (15) | 0.6322 (3) | 0.42626 (15) | 0.0155 (5) |
| C12 | 0.53083 (15) | 0.3119 (4) | 0.62096 (16) | 0.0196 (5) |
| H8A | 0.488167 | 0.407825 | 0.611530 | 0.029* |

| | | | | |
|---|---|---|---|---|
| H8B | 0.515078 | 0.205199 | 0.644608 | 0.029* |
| H8C | 0.534144 | 0.276943 | 0.570466 | 0.029* |
| C16 | 0.81928 (16) | 1.1913 (3) | 0.30107 (15) | 0.0170 (5) |
| H16A | 0.764854 | 1.140422 | 0.265770 | 0.025* |
| H16B | 0.835344 | 1.291111 | 0.273954 | 0.025* |
| H16C | 0.814374 | 1.238204 | 0.349352 | 0.025* |
| C13 | 0.88640 (14) | 1.0428 (3) | 0.32301 (14) | 0.0126 (5) |
| C15 | 0.89362 (16) | 0.9645 (3) | 0.24873 (15) | 0.0186 (5) |
| H15A | 0.935772 | 0.866340 | 0.263706 | 0.028* |
| H15B | 0.911020 | 1.061099 | 0.221125 | 0.028* |
| H15C | 0.838699 | 0.915498 | 0.213542 | 0.028* |
| C6 | 0.90270 (15) | 0.7277 (3) | 0.38943 (15) | 0.0157 (5) |
| C14 | 0.97108 (15) | 1.1159 (4) | 0.38186 (16) | 0.0195 (5) |
| H14A | 0.964657 | 1.157067 | 0.430264 | 0.029* |
| H14B | 0.989184 | 1.218801 | 0.357887 | 0.029* |
| H14C | 1.013621 | 1.018734 | 0.395112 | 0.029* |
| H5 | 0.7461 (15) | 0.464 (3) | 0.6249 (15) | 0.006 (6)* |
| H4 | 0.5430 (18) | 0.717 (4) | 0.6210 (17) | 0.023 (8)* |
| H12 | 0.7552 (15) | 0.985 (3) | 0.3754 (14) | 0.003 (6)* |
| H11 | 0.9505 (17) | 0.698 (4) | 0.3796 (16) | 0.018 (7)* |
| H3 | 0.6180 (17) | 0.910 (4) | 0.5485 (17) | 0.018 (7)* |
| H10 | 0.8680 (18) | 0.521 (4) | 0.4505 (18) | 0.028 (8)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br2 | 0.01224 (11) | 0.01866 (13) | 0.02260 (14) | −0.00149 (9) | 0.00642 (10) | 0.00053 (10) |
| Br1 | 0.02064 (13) | 0.01617 (12) | 0.01448 (13) | −0.00222 (9) | 0.00658 (10) | 0.00156 (9) |
| O2 | 0.0199 (9) | 0.0299 (11) | 0.0227 (11) | 0.0067 (8) | 0.0046 (8) | −0.0070 (8) |
| O1 | 0.0261 (10) | 0.0346 (11) | 0.0234 (11) | 0.0008 (9) | 0.0120 (8) | −0.0035 (9) |
| N1 | 0.0115 (9) | 0.0117 (9) | 0.0082 (9) | −0.0001 (7) | 0.0063 (7) | 0.0017 (7) |
| N2 | 0.0120 (9) | 0.0141 (9) | 0.0088 (10) | −0.0008 (7) | 0.0059 (8) | 0.0006 (8) |
| N3 | 0.0135 (9) | 0.0113 (9) | 0.0118 (10) | −0.0022 (7) | 0.0078 (8) | 0.0015 (7) |
| N4 | 0.0129 (9) | 0.0103 (9) | 0.0098 (10) | −0.0010 (7) | 0.0068 (8) | 0.0018 (7) |
| C1 | 0.0114 (10) | 0.0116 (11) | 0.0084 (11) | 0.0009 (9) | 0.0054 (9) | 0.0002 (8) |
| C9 | 0.0148 (11) | 0.0132 (11) | 0.0103 (11) | −0.0025 (9) | 0.0078 (9) | 0.0027 (9) |
| C7 | 0.0146 (11) | 0.0155 (11) | 0.0094 (11) | −0.0034 (9) | 0.0075 (9) | 0.0031 (9) |
| C4 | 0.0125 (10) | 0.0127 (11) | 0.0087 (11) | −0.0010 (9) | 0.0056 (9) | 0.0005 (9) |
| C3 | 0.0170 (12) | 0.0142 (12) | 0.0157 (13) | 0.0041 (9) | 0.0079 (10) | 0.0038 (10) |
| C10 | 0.0214 (12) | 0.0145 (11) | 0.0168 (13) | 0.0004 (9) | 0.0110 (10) | 0.0029 (10) |
| C2 | 0.0150 (11) | 0.0157 (12) | 0.0182 (13) | 0.0048 (9) | 0.0094 (10) | 0.0032 (10) |
| C8 | 0.0135 (11) | 0.0177 (12) | 0.0121 (12) | −0.0047 (9) | 0.0085 (9) | 0.0008 (9) |
| C11 | 0.0228 (12) | 0.0200 (12) | 0.0166 (13) | 0.0004 (10) | 0.0149 (10) | 0.0027 (10) |
| C5 | 0.0192 (12) | 0.0108 (11) | 0.0182 (13) | 0.0020 (9) | 0.0092 (10) | 0.0024 (9) |
| C12 | 0.0157 (12) | 0.0218 (13) | 0.0207 (14) | −0.0074 (10) | 0.0065 (10) | 0.0012 (10) |
| C16 | 0.0217 (12) | 0.0160 (12) | 0.0179 (13) | 0.0024 (10) | 0.0127 (10) | 0.0053 (10) |
| C13 | 0.0143 (11) | 0.0132 (11) | 0.0133 (12) | −0.0032 (9) | 0.0085 (9) | 0.0034 (9) |
| C15 | 0.0240 (13) | 0.0212 (13) | 0.0166 (13) | −0.0010 (10) | 0.0144 (11) | 0.0019 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C6 | 0.0173 (12) | 0.0140 (11) | 0.0200 (13) | 0.0027 (9) | 0.0120 (10) | 0.0014 (10) |
| C14 | 0.0164 (12) | 0.0215 (13) | 0.0199 (13) | −0.0055 (10) | 0.0063 (10) | 0.0031 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O2—H2C | 0.8695 | C10—H9B | 0.9800 |
| O2—H2D | 0.8698 | C10—H9C | 0.9800 |
| O1—H1C | 0.8699 | C2—H4 | 0.94 (3) |
| O1—H1D | 0.8697 | C8—H2A | 0.9900 |
| N1—C1 | 1.327 (3) | C8—H2B | 0.9900 |
| N1—C9 | 1.505 (3) | C11—H7A | 0.9800 |
| N1—C2 | 1.388 (3) | C11—H7B | 0.9800 |
| N2—C1 | 1.331 (3) | C11—H7C | 0.9800 |
| N2—C7 | 1.468 (3) | C5—C6 | 1.352 (3) |
| N2—C3 | 1.384 (3) | C5—H10 | 0.91 (3) |
| N3—C4 | 1.333 (3) | C12—H8A | 0.9800 |
| N3—C8 | 1.468 (3) | C12—H8B | 0.9800 |
| N3—C5 | 1.381 (3) | C12—H8C | 0.9800 |
| N4—C4 | 1.330 (3) | C16—H16A | 0.9800 |
| N4—C13 | 1.503 (3) | C16—H16B | 0.9800 |
| N4—C6 | 1.384 (3) | C16—H16C | 0.9800 |
| C1—H5 | 0.91 (2) | C16—C13 | 1.520 (3) |
| C9—C10 | 1.520 (3) | C13—C15 | 1.522 (3) |
| C9—C11 | 1.526 (3) | C13—C14 | 1.531 (3) |
| C9—C12 | 1.528 (3) | C15—H15A | 0.9800 |
| C7—H1A | 0.9900 | C15—H15B | 0.9800 |
| C7—H1B | 0.9900 | C15—H15C | 0.9800 |
| C7—C8 | 1.518 (3) | C6—H11 | 0.93 (3) |
| C4—H12 | 0.91 (2) | C14—H14A | 0.9800 |
| C3—C2 | 1.349 (3) | C14—H14B | 0.9800 |
| C3—H3 | 0.90 (3) | C14—H14C | 0.9800 |
| C10—H9A | 0.9800 | | |

| | | | |
|---|---|---|---|
| H2C—O2—H2D | 104.5 | N3—C8—H2B | 109.7 |
| H1C—O1—H1D | 109.5 | C7—C8—H2A | 109.7 |
| C1—N1—C9 | 126.71 (19) | C7—C8—H2B | 109.7 |
| C1—N1—C2 | 108.21 (19) | H2A—C8—H2B | 108.2 |
| C2—N1—C9 | 125.02 (18) | C9—C11—H7A | 109.5 |
| C1—N2—C7 | 124.95 (19) | C9—C11—H7B | 109.5 |
| C1—N2—C3 | 108.54 (19) | C9—C11—H7C | 109.5 |
| C3—N2—C7 | 126.4 (2) | H7A—C11—H7B | 109.5 |
| C4—N3—C8 | 124.51 (19) | H7A—C11—H7C | 109.5 |
| C4—N3—C5 | 108.75 (19) | H7B—C11—H7C | 109.5 |
| C5—N3—C8 | 126.7 (2) | N3—C5—H10 | 118.4 (19) |
| C4—N4—C13 | 125.94 (19) | C6—C5—N3 | 106.7 (2) |
| C4—N4—C6 | 108.16 (19) | C6—C5—H10 | 134.9 (19) |
| C6—N4—C13 | 125.85 (19) | C9—C12—H8A | 109.5 |
| N1—C1—N2 | 109.02 (19) | C9—C12—H8B | 109.5 |

| | | | |
|---|---|---|---|
| N1—C1—H5 | 126.1 (16) | C9—C12—H8C | 109.5 |
| N2—C1—H5 | 124.9 (16) | H8A—C12—H8B | 109.5 |
| N1—C9—C10 | 108.60 (18) | H8A—C12—H8C | 109.5 |
| N1—C9—C11 | 107.87 (18) | H8B—C12—H8C | 109.5 |
| N1—C9—C12 | 107.13 (18) | H16A—C16—H16B | 109.5 |
| C10—C9—C11 | 110.2 (2) | H16A—C16—H16C | 109.5 |
| C10—C9—C12 | 110.8 (2) | H16B—C16—H16C | 109.5 |
| C11—C9—C12 | 112.13 (19) | C13—C16—H16A | 109.5 |
| N2—C7—H1A | 109.7 | C13—C16—H16B | 109.5 |
| N2—C7—H1B | 109.7 | C13—C16—H16C | 109.5 |
| N2—C7—C8 | 109.74 (18) | N4—C13—C16 | 108.52 (18) |
| H1A—C7—H1B | 108.2 | N4—C13—C15 | 108.11 (19) |
| C8—C7—H1A | 109.7 | N4—C13—C14 | 107.00 (19) |
| C8—C7—H1B | 109.7 | C16—C13—C15 | 110.4 (2) |
| N3—C4—H12 | 124.6 (15) | C16—C13—C14 | 110.6 (2) |
| N4—C4—N3 | 108.8 (2) | C15—C13—C14 | 112.0 (2) |
| N4—C4—H12 | 126.5 (15) | C13—C15—H15A | 109.5 |
| N2—C3—H3 | 120.5 (17) | C13—C15—H15B | 109.5 |
| C2—C3—N2 | 106.9 (2) | C13—C15—H15C | 109.5 |
| C2—C3—H3 | 132.5 (17) | H15A—C15—H15B | 109.5 |
| C9—C10—H9A | 109.5 | H15A—C15—H15C | 109.5 |
| C9—C10—H9B | 109.5 | H15B—C15—H15C | 109.5 |
| C9—C10—H9C | 109.5 | N4—C6—H11 | 121.8 (17) |
| H9A—C10—H9B | 109.5 | C5—C6—N4 | 107.6 (2) |
| H9A—C10—H9C | 109.5 | C5—C6—H11 | 130.7 (17) |
| H9B—C10—H9C | 109.5 | C13—C14—H14A | 109.5 |
| N1—C2—H4 | 120.4 (18) | C13—C14—H14B | 109.5 |
| C3—C2—N1 | 107.3 (2) | C13—C14—H14C | 109.5 |
| C3—C2—H4 | 132.3 (17) | H14A—C14—H14B | 109.5 |
| N3—C8—C7 | 109.68 (18) | H14A—C14—H14C | 109.5 |
| N3—C8—H2A | 109.7 | H14B—C14—H14C | 109.5 |

| | | | |
|---|---|---|---|
| N2—C7—C8—N3 | −176.23 (18) | C4—N4—C6—C5 | 0.0 (3) |
| N2—C3—C2—N1 | −0.2 (3) | C3—N2—C1—N1 | −0.5 (3) |
| N3—C5—C6—N4 | 0.2 (3) | C3—N2—C7—C8 | −86.8 (3) |
| C1—N1—C9—C10 | 2.3 (3) | C2—N1—C1—N2 | 0.4 (3) |
| C1—N1—C9—C11 | 121.7 (2) | C2—N1—C9—C10 | 179.3 (2) |
| C1—N1—C9—C12 | −117.4 (2) | C2—N1—C9—C11 | −61.3 (3) |
| C1—N1—C2—C3 | −0.1 (3) | C2—N1—C9—C12 | 59.6 (3) |
| C1—N2—C7—C8 | 88.3 (3) | C8—N3—C4—N4 | 178.2 (2) |
| C1—N2—C3—C2 | 0.5 (3) | C8—N3—C5—C6 | −178.1 (2) |
| C9—N1—C1—N2 | 177.7 (2) | C5—N3—C4—N4 | 0.4 (3) |
| C9—N1—C2—C3 | −177.5 (2) | C5—N3—C8—C7 | 88.4 (3) |
| C7—N2—C1—N1 | −176.37 (19) | C13—N4—C4—N3 | −177.8 (2) |
| C7—N2—C3—C2 | 176.3 (2) | C13—N4—C6—C5 | 177.6 (2) |
| C4—N3—C8—C7 | −88.9 (3) | C6—N4—C4—N3 | −0.3 (3) |
| C4—N3—C5—C6 | −0.4 (3) | C6—N4—C13—C16 | 176.4 (2) |
| C4—N4—C13—C16 | −6.5 (3) | C6—N4—C13—C15 | 56.6 (3) |

| | | | |
|---|---|---|---|
| C4—N4—C13—C15 | −126.3 (2) | C6—N4—C13—C14 | −64.3 (3) |
| C4—N4—C13—C14 | 112.8 (2) | | |

**1,1′-Methylenebis[3-(2,4,6-trimethylphenyl)imidazolium] dibromide dihydrate (at01019_0ma)**

*Crystal data*

$C_{25}H_{30}N_4^{2+}\cdot 2Br^-\cdot 2H_2O$
$M_r$ = 582.38
Orthorhombic, *Pccn*
$a$ = 21.5695 (6) Å
$b$ = 28.3385 (6) Å
$c$ = 8.9401 (2) Å
$V$ = 5464.6 (2) Å$^3$
$Z$ = 8
$F(000)$ = 2384
$D_x$ = 1.416 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9959 reflections
$\theta$ = 2.6–39.4°
$\mu$ = 2.99 mm$^{-1}$
$T$ = 112 K
Prism, clear colourless
0.4 × 0.3 × 0.25 mm

*Data collection*

Bruker Venture Kappa D diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.386, $T_{max}$ = 0.748
39085 measured reflections
5954 independent reflections
5530 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.035
$\theta_{max}$ = 27.1°, $\theta_{min}$ = 2.6°
$h$ = −24→27
$k$ = −31→36
$l$ = −11→11

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.066
$S$ = 1.19
5954 reflections
338 parameters
0 restraints
Primary atom site location: iterative
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0149P)^2 + 6.9269P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.42 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.54 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.

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Br1 | 0.32147 (2) | 0.59206 (2) | 0.51936 (2) | 0.01792 (6) | |
| Br2 | 0.33241 (2) | 0.42996 (2) | 0.77256 (2) | 0.01874 (6) | |
| N2 | 0.14868 (8) | 0.40218 (6) | 0.76624 (19) | 0.0134 (3) | |
| N3 | 0.17753 (8) | 0.54615 (6) | 0.5774 (2) | 0.0167 (4) | |
| N1 | 0.17956 (8) | 0.47256 (6) | 0.7130 (2) | 0.0158 (4) | |
| N4 | 0.14048 (8) | 0.61532 (6) | 0.53485 (19) | 0.0151 (3) | |
| C4 | 0.17963 (9) | 0.42757 (7) | 0.6667 (2) | 0.0165 (4) | |
| H4 | 0.198554 | 0.415943 | 0.578146 | 0.020* | |

| | | | | | |
|---|---|---|---|---|---|
| C16 | 0.17313 (9) | 0.59006 (7) | 0.6302 (2) | 0.0154 (4) | |
| H16 | 0.190588 | 0.601214 | 0.721117 | 0.018* | |
| C17 | 0.12153 (9) | 0.66386 (7) | 0.5581 (2) | 0.0146 (4) | |
| C5 | 0.13900 (9) | 0.35172 (7) | 0.7556 (2) | 0.0141 (4) | |
| O2A | 0.4650 (10) | 0.5643 (7) | 0.601 (3) | 0.037 (3) | 0.47 (9) |
| H2AA | 0.482702 | 0.563311 | 0.513609 | 0.055* | 0.47 (9) |
| H2AB | 0.427586 | 0.574062 | 0.582766 | 0.055* | 0.47 (9) |
| C12 | 0.22444 (10) | 0.34048 (8) | 0.9479 (2) | 0.0201 (4) | |
| H12A | 0.256440 | 0.357156 | 0.890780 | 0.030* | |
| H12B | 0.243324 | 0.314106 | 1.002226 | 0.030* | |
| H12C | 0.205240 | 0.362270 | 1.019314 | 0.030* | |
| C14 | 0.14765 (13) | 0.54398 (8) | 0.4406 (3) | 0.0275 (5) | |
| C18 | 0.07474 (9) | 0.67224 (7) | 0.6624 (2) | 0.0150 (4) | |
| C22 | 0.15021 (10) | 0.69938 (7) | 0.4754 (2) | 0.0179 (4) | |
| C6 | 0.17572 (9) | 0.32189 (7) | 0.8424 (2) | 0.0153 (4) | |
| C24 | 0.04581 (10) | 0.63259 (7) | 0.7507 (2) | 0.0190 (4) | |
| H24A | 0.037277 | 0.605939 | 0.683916 | 0.028* | |
| H24B | 0.006967 | 0.643518 | 0.795745 | 0.028* | |
| H24C | 0.074401 | 0.622543 | 0.829693 | 0.028* | |
| C3 | 0.12848 (12) | 0.43164 (8) | 0.8801 (3) | 0.0244 (5) | |
| C10 | 0.09279 (10) | 0.33558 (7) | 0.6589 (2) | 0.0163 (4) | |
| C15 | 0.12434 (13) | 0.58713 (8) | 0.4143 (3) | 0.0272 (5) | |
| C1 | 0.21637 (10) | 0.50965 (7) | 0.6432 (3) | 0.0231 (5) | |
| H1A | 0.243891 | 0.524043 | 0.719194 | 0.028* | |
| H1B | 0.242843 | 0.495638 | 0.564401 | 0.028* | |
| C19 | 0.05623 (10) | 0.71864 (7) | 0.6822 (2) | 0.0174 (4) | |
| H19 | 0.024420 | 0.725449 | 0.752452 | 0.021* | |
| C11 | 0.05222 (11) | 0.36931 (8) | 0.5741 (3) | 0.0242 (5) | |
| H11A | 0.036347 | 0.393487 | 0.642452 | 0.036* | |
| H11B | 0.017393 | 0.352060 | 0.529724 | 0.036* | |
| H11C | 0.076445 | 0.384406 | 0.494617 | 0.036* | |
| O1A | 0.47220 (10) | 0.47135 (8) | 0.6838 (4) | 0.0715 (9) | |
| H1AA | 0.487824 | 0.450597 | 0.622561 | 0.107* | |
| H1AB | 0.436751 | 0.459386 | 0.710574 | 0.107* | |
| C7 | 0.16563 (9) | 0.27361 (7) | 0.8269 (2) | 0.0175 (4) | |
| H7 | 0.189642 | 0.252345 | 0.885177 | 0.021* | |
| C2 | 0.14808 (12) | 0.47542 (8) | 0.8472 (3) | 0.0245 (5) | |
| C20 | 0.08292 (10) | 0.75565 (7) | 0.6021 (2) | 0.0182 (4) | |
| C23 | 0.20108 (11) | 0.68858 (8) | 0.3644 (3) | 0.0263 (5) | |
| H23A | 0.236552 | 0.674719 | 0.416963 | 0.040* | |
| H23B | 0.214017 | 0.717788 | 0.314740 | 0.040* | |
| H23C | 0.185662 | 0.666212 | 0.289523 | 0.040* | |
| C8 | 0.12146 (10) | 0.25546 (7) | 0.7288 (2) | 0.0184 (4) | |
| C9 | 0.08556 (10) | 0.28686 (7) | 0.6465 (2) | 0.0179 (4) | |
| H9 | 0.055181 | 0.274754 | 0.579845 | 0.021* | |
| C13 | 0.11192 (11) | 0.20288 (7) | 0.7166 (3) | 0.0243 (5) | |
| H13A | 0.152068 | 0.186833 | 0.723425 | 0.036* | |
| H13B | 0.092477 | 0.195470 | 0.620360 | 0.036* | |

| | | | | | |
|---|---|---|---|---|---|
| H13C | 0.085012 | 0.192160 | 0.798149 | 0.036* | |
| C21 | 0.12978 (10) | 0.74543 (7) | 0.5009 (2) | 0.0197 (4) | |
| H21 | 0.148577 | 0.770574 | 0.447203 | 0.024* | |
| C25 | 0.06032 (11) | 0.80563 (7) | 0.6251 (3) | 0.0256 (5) | |
| H25A | 0.020408 | 0.809802 | 0.574412 | 0.038* | |
| H25B | 0.090640 | 0.827784 | 0.583474 | 0.038* | |
| H25C | 0.055261 | 0.811696 | 0.732324 | 0.038* | |
| H2 | 0.1460 (13) | 0.5020 (10) | 0.892 (3) | 0.031* | |
| H15 | 0.1018 (13) | 0.5989 (9) | 0.332 (3) | 0.031* | |
| H3 | 0.1080 (13) | 0.4191 (10) | 0.963 (3) | 0.031* | |
| H14 | 0.1479 (13) | 0.5182 (10) | 0.388 (3) | 0.031* | |
| O2 | 0.4729 (8) | 0.5614 (8) | 0.556 (4) | 0.043 (5) | 0.53 (9) |
| H2A | 0.438 (4) | 0.569 (4) | 0.542 (11) | 0.064* | 0.53 (9) |
| H2B | 0.465 (4) | 0.542 (3) | 0.606 (11) | 0.064* | 0.53 (9) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.01793 (11) | 0.01900 (10) | 0.01682 (11) | −0.00262 (8) | 0.00203 (8) | −0.00139 (8) |
| Br2 | 0.02215 (11) | 0.01532 (10) | 0.01876 (11) | −0.00184 (8) | 0.00044 (8) | −0.00160 (8) |
| N2 | 0.0173 (8) | 0.0108 (8) | 0.0120 (8) | −0.0006 (6) | 0.0010 (6) | −0.0006 (6) |
| N3 | 0.0177 (9) | 0.0101 (8) | 0.0222 (9) | 0.0009 (6) | 0.0016 (7) | 0.0035 (7) |
| N1 | 0.0145 (8) | 0.0116 (8) | 0.0213 (9) | 0.0005 (6) | 0.0008 (7) | 0.0025 (7) |
| N4 | 0.0207 (9) | 0.0114 (8) | 0.0133 (8) | 0.0006 (6) | −0.0008 (7) | 0.0006 (7) |
| C4 | 0.0157 (10) | 0.0147 (9) | 0.0190 (10) | 0.0021 (8) | 0.0023 (8) | 0.0000 (8) |
| C16 | 0.0150 (10) | 0.0125 (9) | 0.0186 (10) | −0.0017 (7) | −0.0002 (8) | 0.0012 (8) |
| C17 | 0.0179 (10) | 0.0113 (9) | 0.0147 (10) | 0.0014 (7) | −0.0043 (8) | −0.0008 (8) |
| C5 | 0.0186 (10) | 0.0101 (9) | 0.0135 (10) | −0.0020 (7) | 0.0038 (8) | 0.0000 (7) |
| O2A | 0.026 (5) | 0.040 (4) | 0.045 (6) | 0.008 (4) | 0.005 (4) | 0.005 (5) |
| C12 | 0.0208 (11) | 0.0196 (10) | 0.0200 (11) | −0.0019 (8) | −0.0023 (9) | 0.0016 (9) |
| C14 | 0.0443 (15) | 0.0135 (10) | 0.0248 (12) | 0.0035 (10) | −0.0058 (11) | −0.0070 (9) |
| C18 | 0.0174 (10) | 0.0128 (9) | 0.0148 (10) | −0.0008 (7) | −0.0047 (8) | 0.0020 (8) |
| C22 | 0.0198 (11) | 0.0149 (10) | 0.0192 (10) | −0.0008 (8) | −0.0009 (8) | 0.0011 (8) |
| C6 | 0.0135 (10) | 0.0168 (9) | 0.0157 (10) | −0.0010 (7) | 0.0034 (8) | 0.0016 (8) |
| C24 | 0.0206 (11) | 0.0157 (10) | 0.0205 (11) | 0.0016 (8) | 0.0014 (9) | 0.0045 (8) |
| C3 | 0.0376 (14) | 0.0183 (11) | 0.0174 (11) | 0.0000 (9) | 0.0088 (10) | −0.0005 (9) |
| C10 | 0.0177 (10) | 0.0163 (10) | 0.0150 (10) | −0.0026 (8) | 0.0008 (8) | 0.0027 (8) |
| C15 | 0.0446 (15) | 0.0182 (11) | 0.0188 (11) | 0.0055 (10) | −0.0107 (11) | −0.0043 (9) |
| C1 | 0.0170 (11) | 0.0122 (10) | 0.0402 (14) | 0.0011 (8) | 0.0022 (10) | 0.0103 (9) |
| C19 | 0.0182 (10) | 0.0151 (10) | 0.0188 (10) | 0.0023 (8) | −0.0018 (8) | −0.0007 (8) |
| C11 | 0.0257 (12) | 0.0202 (11) | 0.0266 (12) | −0.0037 (9) | −0.0083 (10) | 0.0042 (9) |
| O1A | 0.0296 (12) | 0.0545 (14) | 0.130 (3) | 0.0055 (10) | 0.0180 (14) | 0.0468 (16) |
| C7 | 0.0168 (10) | 0.0147 (9) | 0.0208 (10) | 0.0018 (8) | 0.0026 (8) | 0.0041 (8) |
| C2 | 0.0364 (14) | 0.0154 (10) | 0.0216 (12) | 0.0015 (9) | 0.0050 (10) | −0.0040 (9) |
| C20 | 0.0212 (11) | 0.0107 (9) | 0.0227 (11) | 0.0007 (8) | −0.0062 (9) | −0.0007 (8) |
| C23 | 0.0283 (13) | 0.0216 (11) | 0.0291 (13) | 0.0004 (9) | 0.0091 (10) | 0.0042 (10) |
| C8 | 0.0202 (10) | 0.0147 (10) | 0.0201 (10) | −0.0028 (8) | 0.0083 (8) | −0.0002 (8) |
| C9 | 0.0203 (11) | 0.0170 (10) | 0.0164 (10) | −0.0057 (8) | 0.0002 (8) | −0.0013 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C13 | 0.0267 (12) | 0.0148 (10) | 0.0313 (13) | −0.0033 (8) | 0.0054 (10) | −0.0026 (9) |
| C21 | 0.0225 (11) | 0.0125 (9) | 0.0242 (11) | −0.0027 (8) | −0.0021 (9) | 0.0036 (9) |
| C25 | 0.0283 (12) | 0.0120 (10) | 0.0366 (14) | 0.0028 (9) | 0.0002 (10) | −0.0008 (10) |
| O2 | 0.023 (4) | 0.045 (5) | 0.060 (13) | 0.013 (3) | 0.006 (5) | 0.026 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N2—C4 | 1.325 (3) | C3—C2 | 1.343 (3) |
| N2—C5 | 1.448 (2) | C3—H3 | 0.93 (3) |
| N2—C3 | 1.387 (3) | C10—C11 | 1.502 (3) |
| N3—C16 | 1.334 (3) | C10—C9 | 1.394 (3) |
| N3—C14 | 1.384 (3) | C15—H15 | 0.94 (3) |
| N3—C1 | 1.455 (3) | C1—H1A | 0.9900 |
| N1—C4 | 1.340 (3) | C1—H1B | 0.9900 |
| N1—C1 | 1.458 (3) | C19—H19 | 0.9500 |
| N1—C2 | 1.380 (3) | C19—C20 | 1.394 (3) |
| N4—C16 | 1.317 (3) | C11—H11A | 0.9800 |
| N4—C17 | 1.450 (2) | C11—H11B | 0.9800 |
| N4—C15 | 1.386 (3) | C11—H11C | 0.9800 |
| C4—H4 | 0.9500 | O1A—H1AA | 0.8712 |
| C16—H16 | 0.9500 | O1A—H1AB | 0.8701 |
| C17—C18 | 1.394 (3) | C7—H7 | 0.9500 |
| C17—C22 | 1.394 (3) | C7—C8 | 1.394 (3) |
| C5—C6 | 1.394 (3) | C2—H2 | 0.86 (3) |
| C5—C10 | 1.396 (3) | C20—C21 | 1.387 (3) |
| O2A—H2AA | 0.8694 | C20—C25 | 1.512 (3) |
| O2A—H2AB | 0.8679 | C23—H23A | 0.9800 |
| C12—H12A | 0.9800 | C23—H23B | 0.9800 |
| C12—H12B | 0.9800 | C23—H23C | 0.9800 |
| C12—H12C | 0.9800 | C8—C9 | 1.390 (3) |
| C12—C6 | 1.507 (3) | C8—C13 | 1.508 (3) |
| C14—C15 | 1.343 (3) | C9—H9 | 0.9500 |
| C14—H14 | 0.87 (3) | C13—H13A | 0.9800 |
| C18—C24 | 1.508 (3) | C13—H13B | 0.9800 |
| C18—C19 | 1.386 (3) | C13—H13C | 0.9800 |
| C22—C23 | 1.511 (3) | C21—H21 | 0.9500 |
| C22—C21 | 1.396 (3) | C25—H25A | 0.9800 |
| C6—C7 | 1.392 (3) | C25—H25B | 0.9800 |
| C24—H24A | 0.9800 | C25—H25C | 0.9800 |
| C24—H24B | 0.9800 | O2—H2A | 0.79 (9) |
| C24—H24C | 0.9800 | O2—H2B | 0.74 (11) |
| | | | |
| C4—N2—C5 | 124.39 (17) | C14—C15—N4 | 107.1 (2) |
| C4—N2—C3 | 108.93 (17) | C14—C15—H15 | 130.8 (17) |
| C3—N2—C5 | 126.68 (17) | N3—C1—N1 | 111.83 (17) |
| C16—N3—C14 | 108.72 (18) | N3—C1—H1A | 109.3 |
| C16—N3—C1 | 124.13 (19) | N3—C1—H1B | 109.3 |
| C14—N3—C1 | 126.41 (19) | N1—C1—H1A | 109.3 |

| | | | |
|---|---|---|---|
| C4—N1—C1 | 123.56 (19) | N1—C1—H1B | 109.3 |
| C4—N1—C2 | 108.94 (18) | H1A—C1—H1B | 107.9 |
| C2—N1—C1 | 126.71 (19) | C18—C19—H19 | 119.0 |
| C16—N4—C17 | 124.98 (17) | C18—C19—C20 | 122.0 (2) |
| C16—N4—C15 | 108.91 (17) | C20—C19—H19 | 119.0 |
| C15—N4—C17 | 126.00 (18) | C10—C11—H11A | 109.5 |
| N2—C4—N1 | 107.98 (18) | C10—C11—H11B | 109.5 |
| N2—C4—H4 | 126.0 | C10—C11—H11C | 109.5 |
| N1—C4—H4 | 126.0 | H11A—C11—H11B | 109.5 |
| N3—C16—H16 | 125.8 | H11A—C11—H11C | 109.5 |
| N4—C16—N3 | 108.43 (19) | H11B—C11—H11C | 109.5 |
| N4—C16—H16 | 125.8 | H1AA—O1A—H1AB | 104.5 |
| C18—C17—N4 | 117.50 (17) | C6—C7—H7 | 118.9 |
| C22—C17—N4 | 118.93 (18) | C6—C7—C8 | 122.13 (19) |
| C22—C17—C18 | 123.56 (18) | C8—C7—H7 | 118.9 |
| C6—C5—N2 | 118.71 (18) | N1—C2—H2 | 119.2 (19) |
| C6—C5—C10 | 123.44 (18) | C3—C2—N1 | 106.9 (2) |
| C10—C5—N2 | 117.85 (18) | C3—C2—H2 | 133.8 (19) |
| H2AA—O2A—H2AB | 104.6 | C19—C20—C25 | 120.1 (2) |
| H12A—C12—H12B | 109.5 | C21—C20—C19 | 118.61 (19) |
| H12A—C12—H12C | 109.5 | C21—C20—C25 | 121.3 (2) |
| H12B—C12—H12C | 109.5 | C22—C23—H23A | 109.5 |
| C6—C12—H12A | 109.5 | C22—C23—H23B | 109.5 |
| C6—C12—H12B | 109.5 | C22—C23—H23C | 109.5 |
| C6—C12—H12C | 109.5 | H23A—C23—H23B | 109.5 |
| N3—C14—H14 | 121.0 (18) | H23A—C23—H23C | 109.5 |
| C15—C14—N3 | 106.8 (2) | H23B—C23—H23C | 109.5 |
| C15—C14—H14 | 132.2 (19) | C7—C8—C13 | 120.2 (2) |
| C17—C18—C24 | 121.48 (18) | C9—C8—C7 | 118.53 (19) |
| C19—C18—C17 | 117.11 (19) | C9—C8—C13 | 121.2 (2) |
| C19—C18—C24 | 121.41 (19) | C10—C9—H9 | 119.0 |
| C17—C22—C23 | 121.64 (19) | C8—C9—C10 | 122.0 (2) |
| C17—C22—C21 | 116.6 (2) | C8—C9—H9 | 119.0 |
| C21—C22—C23 | 121.72 (19) | C8—C13—H13A | 109.5 |
| C5—C6—C12 | 122.16 (18) | C8—C13—H13B | 109.5 |
| C7—C6—C5 | 116.87 (19) | C8—C13—H13C | 109.5 |
| C7—C6—C12 | 120.96 (19) | H13A—C13—H13B | 109.5 |
| C18—C24—H24A | 109.5 | H13A—C13—H13C | 109.5 |
| C18—C24—H24B | 109.5 | H13B—C13—H13C | 109.5 |
| C18—C24—H24C | 109.5 | C22—C21—H21 | 118.9 |
| H24A—C24—H24B | 109.5 | C20—C21—C22 | 122.1 (2) |
| H24A—C24—H24C | 109.5 | C20—C21—H21 | 118.9 |
| H24B—C24—H24C | 109.5 | C20—C25—H25A | 109.5 |
| N2—C3—H3 | 120.2 (17) | C20—C25—H25B | 109.5 |
| C2—C3—N2 | 107.2 (2) | C20—C25—H25C | 109.5 |
| C2—C3—H3 | 132.4 (17) | H25A—C25—H25B | 109.5 |
| C5—C10—C11 | 121.33 (18) | H25A—C25—H25C | 109.5 |
| C9—C10—C5 | 116.98 (19) | H25B—C25—H25C | 109.5 |

| | | | |
|---|---|---|---|
| C9—C10—C11 | 121.68 (19) | H2A—O2—H2B | 94 (10) |
| N4—C15—H15 | 122.0 (17) | | |
| | | | |
| N2—C5—C6—C12 | 0.8 (3) | C18—C17—C22—C23 | 179.6 (2) |
| N2—C5—C6—C7 | −178.95 (18) | C18—C17—C22—C21 | −0.1 (3) |
| N2—C5—C10—C11 | −2.9 (3) | C18—C19—C20—C21 | −0.7 (3) |
| N2—C5—C10—C9 | 177.94 (18) | C18—C19—C20—C25 | 178.7 (2) |
| N2—C3—C2—N1 | 0.5 (3) | C22—C17—C18—C24 | −179.1 (2) |
| N3—C14—C15—N4 | 0.3 (3) | C22—C17—C18—C19 | 0.4 (3) |
| N4—C17—C18—C24 | 1.4 (3) | C6—C5—C10—C11 | 176.7 (2) |
| N4—C17—C18—C19 | −178.99 (18) | C6—C5—C10—C9 | −2.5 (3) |
| N4—C17—C22—C23 | −1.0 (3) | C6—C7—C8—C9 | −1.5 (3) |
| N4—C17—C22—C21 | 179.30 (18) | C6—C7—C8—C13 | −179.6 (2) |
| C4—N2—C5—C6 | 101.6 (2) | C24—C18—C19—C20 | 179.5 (2) |
| C4—N2—C5—C10 | −78.8 (3) | C3—N2—C4—N1 | −0.4 (2) |
| C4—N2—C3—C2 | −0.1 (3) | C3—N2—C5—C6 | −77.5 (3) |
| C4—N1—C1—N3 | 116.6 (2) | C3—N2—C5—C10 | 102.1 (3) |
| C4—N1—C2—C3 | −0.8 (3) | C10—C5—C6—C12 | −178.8 (2) |
| C16—N3—C14—C15 | −1.2 (3) | C10—C5—C6—C7 | 1.5 (3) |
| C16—N3—C1—N1 | 110.9 (2) | C15—N4—C16—N3 | −1.4 (2) |
| C16—N4—C17—C18 | −72.6 (3) | C15—N4—C17—C18 | 103.3 (3) |
| C16—N4—C17—C22 | 108.0 (2) | C15—N4—C17—C22 | −76.2 (3) |
| C16—N4—C15—C14 | 0.7 (3) | C1—N3—C16—N4 | 172.30 (18) |
| C17—N4—C16—N3 | 175.03 (18) | C1—N3—C14—C15 | −171.6 (2) |
| C17—N4—C15—C14 | −175.7 (2) | C1—N1—C4—N2 | 171.14 (19) |
| C17—C18—C19—C20 | 0.0 (3) | C1—N1—C2—C3 | −170.8 (2) |
| C17—C22—C21—C20 | −0.6 (3) | C19—C20—C21—C22 | 1.0 (3) |
| C5—N2—C4—N1 | −179.63 (18) | C11—C10—C9—C8 | −177.7 (2) |
| C5—N2—C3—C2 | 179.1 (2) | C7—C8—C9—C10 | 0.4 (3) |
| C5—C6—C7—C8 | 0.6 (3) | C2—N1—C4—N2 | 0.7 (2) |
| C5—C10—C9—C8 | 1.5 (3) | C2—N1—C1—N3 | −74.7 (3) |
| C12—C6—C7—C8 | −179.16 (19) | C23—C22—C21—C20 | 179.7 (2) |
| C14—N3—C16—N4 | 1.6 (2) | C13—C8—C9—C10 | 178.5 (2) |
| C14—N3—C1—N1 | −80.1 (3) | C25—C20—C21—C22 | −178.4 (2) |

**1,1′-(Ethane-1,2-diyl)bis[3-(2,4,6-trimethylphenyl)imidazolium] dibromide tetrahydrate (est01041d_0ma)**

*Crystal data*

$C_{26}H_{32}N_4^{2+}\cdot 2Br^-\cdot 4H_2O$
$M_r$ = 632.42
Monoclinic, $P2_1/c$
$a$ = 12.4230 (3) Å
$b$ = 13.1447 (3) Å
$c$ = 9.2780 (2) Å
$\beta$ = 108.379 (1)°
$V$ = 1437.78 (6) Å$^3$
$Z$ = 2
$F(000)$ = 652
$D_x$ = 1.461 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9565 reflections
$\theta$ = 2.3–44.6°
$\mu$ = 2.86 mm$^{-1}$
$T$ = 100 K
Prism, clear colourless
0.15 × 0.15 × 0.05 mm

*Data collection*

Bruker Venture D8 Kappa diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.544, $T_{max}$ = 0.750
28199 measured reflections
3165 independent reflections
3028 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025
$\theta_{max}$ = 27.1°, $\theta_{min}$ = 2.8°
$h$ = −15→15
$k$ = −16→16
$l$ = −11→11

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.044
$S$ = 1.10
3165 reflections
194 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2 + 0.8539P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.29 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.

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br01 | −0.19328 (2) | 0.01828 (2) | 0.22033 (2) | 0.01558 (5) |
| O1 | −0.07000 (10) | 0.23627 (9) | 0.37843 (13) | 0.0268 (2) |
| H1D | −0.1073 (18) | 0.1876 (18) | 0.340 (2) | 0.036 (5)* |
| H1E | −0.0360 (18) | 0.2528 (17) | 0.326 (3) | 0.039 (6)* |
| N1 | 0.28176 (8) | 0.55577 (8) | 0.81318 (11) | 0.0117 (2) |
| N2 | 0.12491 (9) | 0.48768 (8) | 0.67428 (12) | 0.0123 (2) |
| O2 | 0.04964 (10) | 0.29104 (10) | 0.18398 (14) | 0.0276 (2) |
| H2A | 0.0823 (18) | 0.3420 (18) | 0.200 (2) | 0.036 (6)* |
| H2B | 0.016 (2) | 0.2902 (19) | 0.096 (3) | 0.051 (7)* |
| C12 | 0.71245 (12) | 0.75891 (11) | 0.97675 (18) | 0.0250 (3) |
| H1A | 0.736386 | 0.766617 | 0.886291 | 0.037* |
| H1B | 0.768542 | 0.718094 | 1.052694 | 0.037* |
| H1C | 0.706272 | 0.826152 | 1.019087 | 0.037* |
| C6 | 0.59853 (11) | 0.70628 (10) | 0.93381 (15) | 0.0166 (3) |
| C10 | 0.51141 (11) | 0.74146 (10) | 0.98445 (14) | 0.0166 (3) |
| H3 | 0.523920 | 0.800361 | 1.046905 | 0.020* |
| C8 | 0.40605 (11) | 0.69326 (10) | 0.94673 (14) | 0.0148 (2) |
| C9 | 0.39084 (10) | 0.60639 (9) | 0.85679 (13) | 0.0117 (2) |
| C1 | 0.21894 (10) | 0.53490 (9) | 0.67103 (14) | 0.0126 (2) |
| H6 | 0.2362 (13) | 0.5503 (13) | 0.5832 (19) | 0.015 (4)* |
| C7 | 0.03385 (10) | 0.45390 (10) | 0.53959 (14) | 0.0132 (2) |
| H7A | −0.016689 | 0.406014 | 0.569818 | 0.016* |

| | | | | |
|---|---|---|---|---|
| H7B | 0.066579 | 0.418089 | 0.469255 | 0.016* |
| C4 | 0.47678 (10) | 0.56704 (10) | 0.80436 (13) | 0.0128 (2) |
| C5 | 0.57920 (10) | 0.61949 (10) | 0.84337 (14) | 0.0147 (2) |
| H9 | 0.637928 | 0.595239 | 0.807044 | 0.018* |
| C13 | 0.46334 (11) | 0.47141 (10) | 0.71025 (16) | 0.0183 (3) |
| H10A | 0.418593 | 0.486447 | 0.604922 | 0.027* |
| H10B | 0.424390 | 0.419506 | 0.751255 | 0.027* |
| H10C | 0.538291 | 0.446186 | 0.713460 | 0.027* |
| C11 | 0.31461 (12) | 0.73712 (11) | 1.00412 (16) | 0.0225 (3) |
| H11A | 0.240263 | 0.726481 | 0.927945 | 0.034* |
| H11B | 0.327739 | 0.810168 | 1.022662 | 0.034* |
| H11C | 0.316568 | 0.703141 | 1.098930 | 0.034* |
| C3 | 0.12649 (11) | 0.47941 (11) | 0.82365 (15) | 0.0166 (3) |
| H12 | 0.0660 (15) | 0.4502 (14) | 0.8469 (19) | 0.023 (4)* |
| C2 | 0.22470 (11) | 0.52150 (11) | 0.91051 (15) | 0.0162 (3) |
| H13 | 0.2517 (15) | 0.5293 (13) | 1.016 (2) | 0.022 (4)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br01 | 0.01802 (7) | 0.01898 (8) | 0.01231 (7) | −0.00240 (5) | 0.00847 (5) | −0.00121 (5) |
| O1 | 0.0320 (6) | 0.0288 (6) | 0.0207 (5) | −0.0124 (5) | 0.0100 (5) | −0.0066 (5) |
| N1 | 0.0124 (5) | 0.0137 (5) | 0.0093 (5) | 0.0009 (4) | 0.0037 (4) | 0.0012 (4) |
| N2 | 0.0122 (5) | 0.0141 (5) | 0.0108 (5) | −0.0002 (4) | 0.0039 (4) | 0.0020 (4) |
| O2 | 0.0332 (6) | 0.0284 (6) | 0.0201 (6) | −0.0086 (5) | 0.0068 (5) | 0.0010 (5) |
| C12 | 0.0165 (6) | 0.0195 (7) | 0.0338 (8) | −0.0033 (5) | 0.0007 (6) | −0.0009 (6) |
| C6 | 0.0159 (6) | 0.0141 (6) | 0.0158 (6) | −0.0007 (5) | −0.0005 (5) | 0.0031 (5) |
| C10 | 0.0206 (6) | 0.0125 (6) | 0.0133 (6) | 0.0006 (5) | 0.0003 (5) | −0.0027 (5) |
| C8 | 0.0168 (6) | 0.0150 (6) | 0.0112 (5) | 0.0045 (5) | 0.0024 (4) | 0.0008 (5) |
| C9 | 0.0116 (5) | 0.0134 (6) | 0.0087 (5) | −0.0002 (4) | 0.0012 (4) | 0.0018 (4) |
| C1 | 0.0141 (6) | 0.0132 (6) | 0.0109 (6) | −0.0006 (4) | 0.0046 (5) | 0.0007 (4) |
| C7 | 0.0125 (5) | 0.0136 (6) | 0.0120 (5) | −0.0024 (5) | 0.0021 (4) | −0.0005 (5) |
| C4 | 0.0153 (6) | 0.0127 (6) | 0.0094 (5) | 0.0015 (5) | 0.0027 (4) | 0.0008 (5) |
| C5 | 0.0136 (5) | 0.0161 (6) | 0.0140 (6) | 0.0018 (5) | 0.0036 (4) | 0.0020 (5) |
| C13 | 0.0178 (6) | 0.0179 (7) | 0.0200 (6) | −0.0004 (5) | 0.0070 (5) | −0.0070 (5) |
| C11 | 0.0222 (7) | 0.0238 (7) | 0.0219 (7) | 0.0057 (5) | 0.0076 (5) | −0.0074 (6) |
| C3 | 0.0155 (6) | 0.0228 (7) | 0.0127 (6) | 0.0005 (5) | 0.0064 (5) | 0.0050 (5) |
| C2 | 0.0164 (6) | 0.0224 (7) | 0.0109 (6) | 0.0025 (5) | 0.0059 (5) | 0.0036 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—H1D | 0.80 (2) | C8—C11 | 1.5126 (17) |
| O1—H1E | 0.77 (2) | C9—C4 | 1.4042 (17) |
| N1—C9 | 1.4481 (15) | C1—H6 | 0.928 (17) |
| N1—C1 | 1.3322 (16) | C7—C7$^{i}$ | 1.525 (2) |
| N1—C2 | 1.3872 (16) | C7—H7A | 0.9900 |
| N2—C1 | 1.3314 (16) | C7—H7B | 0.9900 |
| N2—C7 | 1.4653 (16) | C4—C5 | 1.3909 (17) |

| | | | |
|---|---|---|---|
| N2—C3 | 1.3841 (16) | C4—C13 | 1.5095 (17) |
| O2—H2A | 0.77 (2) | C5—H9 | 0.9500 |
| O2—H2B | 0.79 (3) | C13—H10A | 0.9800 |
| C12—H1A | 0.9800 | C13—H10B | 0.9800 |
| C12—H1B | 0.9800 | C13—H10C | 0.9800 |
| C12—H1C | 0.9800 | C11—H11A | 0.9800 |
| C12—C6 | 1.5114 (18) | C11—H11B | 0.9800 |
| C6—C10 | 1.3880 (19) | C11—H11C | 0.9800 |
| C6—C5 | 1.3915 (18) | C3—H12 | 0.928 (18) |
| C10—H3 | 0.9500 | C3—C2 | 1.3506 (19) |
| C10—C8 | 1.3959 (18) | C2—H13 | 0.932 (19) |
| C8—C9 | 1.3915 (18) | | |

| | | | |
|---|---|---|---|
| H1D—O1—H1E | 107 (2) | N2—C7—H7A | 109.8 |
| C1—N1—C9 | 125.15 (10) | N2—C7—H7B | 109.8 |
| C1—N1—C2 | 108.51 (11) | C7$^{i}$—C7—H7A | 109.8 |
| C2—N1—C9 | 126.34 (10) | C7$^{i}$—C7—H7B | 109.8 |
| C1—N2—C7 | 124.67 (11) | H7A—C7—H7B | 108.3 |
| C1—N2—C3 | 108.89 (11) | C9—C4—C13 | 123.34 (11) |
| C3—N2—C7 | 126.41 (11) | C5—C4—C9 | 117.41 (11) |
| H2A—O2—H2B | 106 (2) | C5—C4—C13 | 119.25 (11) |
| H1A—C12—H1B | 109.5 | C6—C5—H9 | 118.9 |
| H1A—C12—H1C | 109.5 | C4—C5—C6 | 122.21 (12) |
| H1B—C12—H1C | 109.5 | C4—C5—H9 | 118.9 |
| C6—C12—H1A | 109.5 | C4—C13—H10A | 109.5 |
| C6—C12—H1B | 109.5 | C4—C13—H10B | 109.5 |
| C6—C12—H1C | 109.5 | C4—C13—H10C | 109.5 |
| C10—C6—C12 | 121.57 (12) | H10A—C13—H10B | 109.5 |
| C10—C6—C5 | 118.20 (12) | H10A—C13—H10C | 109.5 |
| C5—C6—C12 | 120.23 (12) | H10B—C13—H10C | 109.5 |
| C6—C10—H3 | 118.9 | C8—C11—H11A | 109.5 |
| C6—C10—C8 | 122.24 (12) | C8—C11—H11B | 109.5 |
| C8—C10—H3 | 118.9 | C8—C11—H11C | 109.5 |
| C10—C8—C11 | 119.19 (12) | H11A—C11—H11B | 109.5 |
| C9—C8—C10 | 117.53 (12) | H11A—C11—H11C | 109.5 |
| C9—C8—C11 | 123.28 (12) | H11B—C11—H11C | 109.5 |
| C8—C9—N1 | 118.87 (11) | N2—C3—H12 | 120.6 (11) |
| C8—C9—C4 | 122.39 (11) | C2—C3—N2 | 106.87 (11) |
| C4—C9—N1 | 118.73 (11) | C2—C3—H12 | 132.6 (11) |
| N1—C1—H6 | 126.8 (10) | N1—C2—H13 | 123.8 (11) |
| N2—C1—N1 | 108.54 (11) | C3—C2—N1 | 107.19 (11) |
| N2—C1—H6 | 124.6 (10) | C3—C2—H13 | 129.0 (11) |
| N2—C7—C7$^{i}$ | 109.28 (13) | | |

| | | | |
|---|---|---|---|
| N1—C9—C4—C5 | 177.64 (10) | C1—N1—C9—C4 | −53.80 (17) |
| N1—C9—C4—C13 | −2.91 (18) | C1—N1—C2—C3 | 0.17 (15) |
| N2—C3—C2—N1 | 0.44 (15) | C1—N2—C7—C7$^{i}$ | −73.94 (17) |
| C12—C6—C10—C8 | −179.51 (12) | C1—N2—C3—C2 | −0.90 (15) |

| | | | |
|---|---|---|---|
| C12—C6—C5—C4 | 178.27 (12) | C7—N2—C1—N1 | 179.04 (11) |
| C6—C10—C8—C9 | 0.85 (19) | C7—N2—C3—C2 | −178.88 (12) |
| C6—C10—C8—C11 | −179.00 (12) | C5—C6—C10—C8 | −0.48 (19) |
| C10—C6—C5—C4 | −0.78 (19) | C13—C4—C5—C6 | −177.92 (12) |
| C10—C8—C9—N1 | −178.79 (11) | C11—C8—C9—N1 | 1.04 (18) |
| C10—C8—C9—C4 | 0.00 (18) | C11—C8—C9—C4 | 179.84 (12) |
| C8—C9—C4—C5 | −1.16 (18) | C3—N2—C1—N1 | 1.01 (14) |
| C8—C9—C4—C13 | 178.30 (12) | C3—N2—C7—C7$^{i}$ | 103.73 (16) |
| C9—N1—C1—N2 | 179.64 (11) | C2—N1—C9—C8 | −54.53 (17) |
| C9—N1—C2—C3 | 179.79 (12) | C2—N1—C9—C4 | 126.64 (13) |
| C9—C4—C5—C6 | 1.56 (18) | C2—N1—C1—N2 | −0.73 (14) |
| C1—N1—C9—C8 | 125.04 (13) | | |

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.