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# 3,3′-Diethyl-1,1′-(ethane-1,2-diyl)dibenzimidazolium dibromide dihydrate

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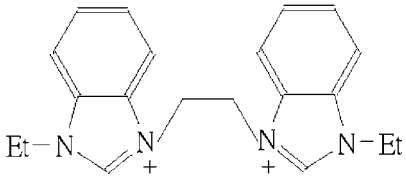
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.026; $wR$ factor = 0.070; data-to-parameter ratio = 15.2.

The title compound, $C_{20}H_{24}N_4^{2+}\cdot 2Br^-\cdot 2H_2O$, was prepared from benzimidazole by stepwise alkylation with ethyl bromide followed by 1,2-bromoethane. The dication lies about a twofold rotation axis through the centre of the ethanyl group that links the two planar benzimidazolium residues. The asymmetric unit also contains a bromide anion and a solvent water molecule. The two benzimidazole ring systems are parallel.

## Related literature

For background to the chemistry of imidazolidenes and metal carbenes based on the imidazole ring, see: Arduengo *et al.* (1991); Fischer *et al.* (2006). For a related structure, see: Liu *et al.* (2003).




## Experimental

### Crystal data

$C_{20}H_{24}N_4^{2+}\cdot 2Br^-\cdot 2H_2O$
$M_r$ = 516.26
Monoclinic, $C2/c$
$a$ = 12.807 (3) Å
$b$ = 11.362 (2) Å
$c$ = 15.297 (3) Å
$\beta$ = 97.912 (4)°
$V$ = 2204.8 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 3.70 mm$^{-1}$
$T$ = 296 (2) K
0.24 × 0.20 × 0.18 mm

### Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.416, $T_{max}$ = 0.514
5494 measured reflections
1951 independent reflections
1683 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.070
$S$ = 1.05
1948 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.29 e Å$^{-3}$

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2352).

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# supplementary materials

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# 3,3'-Diethyl-1,1'-(ethane-1,2-diyl)dibenzimidazolium dibromide dihydrate

**X.-M. Wu, Q.-X. Liu, X.-G. Wang, H.-B. Song and Z.-Y. Zheng**

## Comment

Since the isolation of free stable imidizol-2-ylidene (Imy) (Arduengo *et al.*, 1991), metal carbenes based on imidazole ring have attracted considerable attention, owing to their inherent stability, their interesting characteristics of structure and bonding and their potential on synthesis and catalysts in organic reaction (Fischer *et al.*, 2006). Herein, we wish to report the synthesis and crystal structure of 1,2-bis(1-ethylbenzimidazolium)ethane dibromide. In the molecular structure of title compound (Fig. 1), the dication lies about a twofold axis at the centre of the ethanyl group that links the two planar benzimidazolium residues. The asymmetric unit also contains a bromide anion and a solvent water molecule. The N(1)—C(2), N(1)—C(8), N(2)—C(7) and N(2)—C(8) bond distances are 1.327 (3), 1.395 (3), 1.326 (3) and 1.388 (3) Å, respectively, and the N(2)—C(1)—N(8) bond angle is 108.24 (18)°, which are similar to those observed in 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (Liu *et al.*, 2003).

## Experimental

A THF solution of benzimidazole (2.000 g, 16.9 mmol) was added to a suspension of oil-free sodium hydride (0.480 g, 20.3 mmol) in THF (50 ml) and stirred for 1 h at 60°C. Then a THF (40 ml) solution of ethyl bromide (2.029 g, 18.6 mmol) was added dropwise to above solution. The mixture stirred for 48 h at 60°C and a yellow solution was obtained. The solvent was removed with a rotary evaporator and $H_2O$ (50 ml) added to the residue. Then the solution was extracted with $CH_2Cl_2$ (50 ml), and the extracting solution was dried with anhydrous $MgSO_4$. After removing $CH_2Cl_2$, a pale yellow liquid 1-ethylbenzimidazole was obtained. Yield: 2.220 g (90%). A solution of 1-ethylbenzimidazole (3.423 g, 23.4 mmol) and 1,2-dibromoethane (2.000 g, 10.6 mmol) in THF (50 ml) was stirred for three days under reflux, and a precipitate was formed. The product was filtered and washed with THF. The white powders of 1,2-bis(1-ethylbenzimidazolium)ethane are obtained by recrystallization from methanol/diethyl ether. (2.980 g, 58.3%). Mp: 228–230°C. The crystals of title compound suitable for X-ray diffraction were obtained by evaporating slowly a mixture solution of methanol and water at room temperature.

1,2-bis(3-ethylbenzimidazolium-1-yl)ethane dibromide was obtained as a white solid by recrystallization from methanol/diethyl ether (1:1) (2.980 g, 58.3%). Mp: 228–230°C. Crystals of title compound suitable for X-ray diffraction were obtained by slowly evaporating a solution in methanol/water (5:1) at room temperature.

## Refinement

All H atoms were initially located in a difference Fourier map. and were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, $U_{iso} = 1.2U_{eq}$ (C) for aromatic, d(C—H) = 0.97 Å, $U_{iso} = 1.2U_{eq}$ (C) for $CH_2$, 0.96 Å, $U_{iso} = 1.5U_{eq}$ (C) for $CH_3$ and with d(O—H) = 0.8501 Å, $U_{iso} = 1.5U_{eq}$ (O) for water.

## Figures

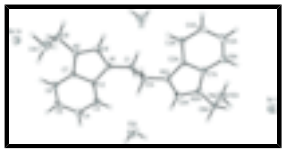


Fig. 1. A perspective view of title compound with anisotropic displacement parameters drawn at the 30% probability level.

## 3,3'-Diethyl-1,1'-(ethane-1,2-diyl)dibenzimidazolium dibromide dihydrate

*Crystal data*

| | |
|---|---|
| $C_{20}H_{24}N_4^{2+}\cdot 2Br^-\cdot 2H_2O$ | $F_{000}$ = 1046.10 |
| $M_r$ = 516.26 | $D_x$ = 1.555 Mg m$^{-3}$ |
| Monoclinic, *C*2/*c* | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: -C 2yc | Cell parameters from 2694 reflections |
| *a* = 12.807 (3) Å | θ = 2.4–26.3º |
| *b* = 11.362 (2) Å | μ = 3.70 mm$^{-1}$ |
| *c* = 15.297 (3) Å | *T* = 296 (2) K |
| β = 97.912 (4)º | Block, colorless |
| *V* = 2204.8 (8) Å$^3$ | 0.24 × 0.20 × 0.18 mm |
| *Z* = 4 | |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD area-detector diffractometer | 1951 independent reflections |
| Radiation source: fine-focus sealed tube | 1683 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.016 |
| *T* = 296(2) K | $\theta_{max}$ = 25.0º |
| φ and ω scans | $\theta_{min}$ = 2.4º |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | *h* = −15→14 |
| $T_{min}$ = 0.416, $T_{max}$ = 0.514 | *k* = −13→11 |
| 5494 measured reflections | *l* = −18→17 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.026 | H-atom parameters constrained |
| $wR(F^2)$ = 0.070 | $w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 2.6765P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| *S* = 1.05 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 1948 reflections | $\Delta\rho_{max}$ = 0.32 e Å$^{-3}$ |

| | |
|---|---|
| 128 parameters | $\Delta\rho_{min} = -0.29$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*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 $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.12265 (2) | 0.55655 (2) | 0.403159 (18) | 0.05085 (12) |
| O1 | 0.87303 (19) | 0.6101 (3) | 0.31595 (17) | 0.0910 (8) |
| H1A | 0.8647 | 0.5982 | 0.2606 | 0.137* |
| H1B | 0.9321 | 0.5892 | 0.3439 | 0.137* |
| N1 | 0.89057 (14) | 0.79681 (17) | 0.52921 (12) | 0.0318 (4) |
| N2 | 1.04995 (14) | 0.77337 (16) | 0.59769 (12) | 0.0316 (4) |
| C1 | 0.79065 (17) | 0.7711 (2) | 0.47218 (15) | 0.0354 (5) |
| H1A' | 0.8022 | 0.7110 | 0.4295 | 0.042* |
| H1B' | 0.7653 | 0.8415 | 0.4402 | 0.042* |
| C2 | 0.92047 (17) | 0.9044 (2) | 0.56882 (14) | 0.0300 (5) |
| C3 | 0.86951 (19) | 1.0121 (2) | 0.56727 (16) | 0.0371 (5) |
| H3 | 0.8008 | 1.0221 | 0.5395 | 0.044* |
| C4 | 0.9267 (2) | 1.1036 (2) | 0.60933 (16) | 0.0407 (6) |
| H4 | 0.8956 | 1.1775 | 0.6096 | 0.049* |
| C5 | 1.0292 (2) | 1.0890 (2) | 0.65129 (16) | 0.0408 (6) |
| H5 | 1.0647 | 1.1535 | 0.6785 | 0.049* |
| C6 | 1.07951 (19) | 0.9822 (2) | 0.65372 (15) | 0.0362 (5) |
| H6 | 1.1480 | 0.9725 | 0.6819 | 0.043* |
| C7 | 1.02248 (16) | 0.8893 (2) | 0.61171 (14) | 0.0285 (5) |
| C8 | 0.96988 (18) | 0.7218 (2) | 0.54795 (16) | 0.0350 (5) |
| H8 | 0.9694 | 0.6440 | 0.5289 | 0.042* |
| C9 | 1.15098 (19) | 0.7166 (2) | 0.63180 (18) | 0.0440 (6) |
| H9A | 1.2087 | 0.7654 | 0.6179 | 0.053* |
| H9B | 1.1556 | 0.6412 | 0.6028 | 0.053* |
| C10 | 1.1618 (3) | 0.6980 (3) | 0.7299 (2) | 0.0688 (9) |
| H10A | 1.1574 | 0.7725 | 0.7588 | 0.103* |
| H10B | 1.2288 | 0.6622 | 0.7499 | 0.103* |
| H10C | 1.1063 | 0.6475 | 0.7437 | 0.103* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.05252 (19) | 0.04308 (18) | 0.05509 (19) | 0.00123 (12) | 0.00082 (13) | 0.00284 (12) |
| O1 | 0.0695 (16) | 0.120 (2) | 0.0827 (17) | 0.0219 (16) | 0.0073 (13) | −0.0388 (16) |
| N1 | 0.0247 (9) | 0.0324 (10) | 0.0373 (10) | −0.0033 (8) | 0.0009 (8) | −0.0024 (8) |
| N2 | 0.0233 (9) | 0.0309 (10) | 0.0401 (11) | 0.0008 (8) | 0.0016 (8) | 0.0004 (8) |
| C1 | 0.0313 (12) | 0.0438 (14) | 0.0299 (12) | −0.0060 (10) | 0.0002 (10) | −0.0037 (10) |
| C2 | 0.0275 (11) | 0.0319 (12) | 0.0307 (11) | −0.0018 (9) | 0.0044 (9) | −0.0014 (9) |
| C3 | 0.0354 (13) | 0.0377 (13) | 0.0377 (12) | 0.0085 (10) | 0.0038 (10) | 0.0017 (11) |
| C4 | 0.0529 (15) | 0.0303 (12) | 0.0405 (14) | 0.0050 (12) | 0.0122 (12) | −0.0005 (11) |
| C5 | 0.0485 (15) | 0.0370 (13) | 0.0386 (13) | −0.0123 (11) | 0.0123 (11) | −0.0099 (11) |
| C6 | 0.0314 (12) | 0.0409 (14) | 0.0358 (12) | −0.0074 (10) | 0.0032 (10) | −0.0037 (10) |
| C7 | 0.0262 (11) | 0.0311 (12) | 0.0284 (11) | −0.0012 (9) | 0.0049 (9) | 0.0012 (9) |
| C8 | 0.0339 (12) | 0.0286 (12) | 0.0424 (13) | −0.0027 (10) | 0.0054 (10) | −0.0029 (10) |
| C9 | 0.0287 (12) | 0.0436 (14) | 0.0580 (16) | 0.0094 (11) | 0.0003 (11) | 0.0021 (12) |
| C10 | 0.064 (2) | 0.072 (2) | 0.065 (2) | 0.0172 (17) | −0.0123 (16) | 0.0157 (17) |

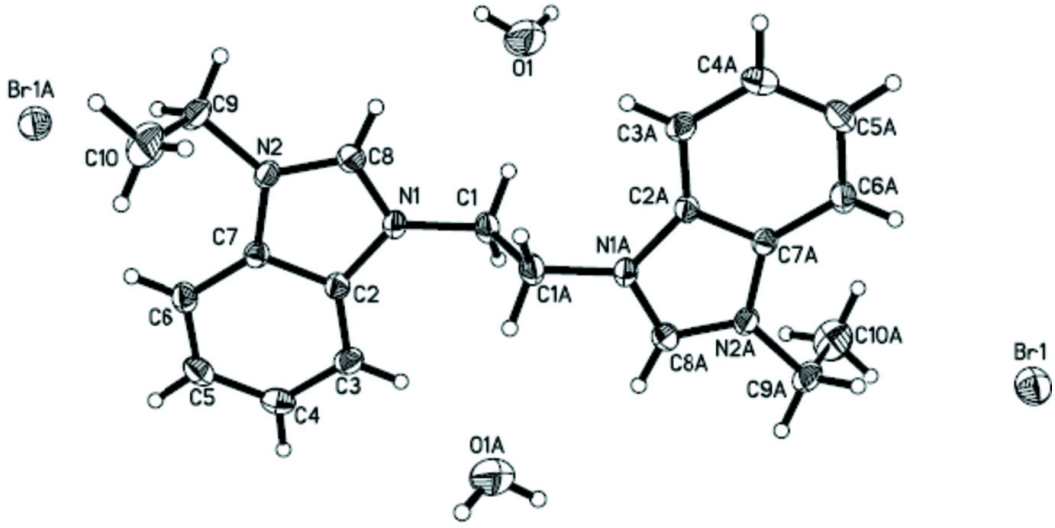
*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—H1A | 0.8501 | C3—H3 | 0.9300 |
| O1—H1B | 0.8501 | C4—C5 | 1.390 (4) |
| N1—C8 | 1.327 (3) | C4—H4 | 0.9300 |
| N1—C2 | 1.395 (3) | C5—C6 | 1.371 (4) |
| N1—C1 | 1.475 (3) | C5—H5 | 0.9300 |
| N2—C8 | 1.326 (3) | C6—C7 | 1.389 (3) |
| N2—C7 | 1.388 (3) | C6—H6 | 0.9300 |
| N2—C9 | 1.475 (3) | C8—H8 | 0.9300 |
| C1—C1$^{i}$ | 1.511 (5) | C9—C10 | 1.503 (4) |
| C1—H1A' | 0.9700 | C9—H9A | 0.9700 |
| C1—H1B' | 0.9700 | C9—H9B | 0.9700 |
| C2—C3 | 1.386 (3) | C10—H10A | 0.9600 |
| C2—C7 | 1.389 (3) | C10—H10B | 0.9600 |
| C3—C4 | 1.378 (4) | C10—H10C | 0.9600 |
| H1A—O1—H1B | 116.0 | C6—C5—H5 | 119.1 |
| C8—N1—C2 | 108.24 (18) | C4—C5—H5 | 119.1 |
| C8—N1—C1 | 125.2 (2) | C5—C6—C7 | 116.4 (2) |
| C2—N1—C1 | 126.48 (19) | C5—C6—H6 | 121.8 |
| C8—N2—C7 | 108.40 (18) | C7—C6—H6 | 121.8 |
| C8—N2—C9 | 125.5 (2) | N2—C7—C2 | 106.62 (19) |
| C7—N2—C9 | 126.10 (19) | N2—C7—C6 | 131.6 (2) |
| N1—C1—C1$^{i}$ | 109.8 (2) | C2—C7—C6 | 121.7 (2) |
| N1—C1—H1A' | 109.7 | N2—C8—N1 | 110.4 (2) |
| C1$^{i}$—C1—H1A' | 109.7 | N2—C8—H8 | 124.8 |
| N1—C1—H1B' | 109.7 | N1—C8—H8 | 124.8 |
| C1$^{i}$—C1—H1B' | 109.7 | N2—C9—C10 | 111.7 (2) |
| H1A'—C1—H1B' | 108.2 | N2—C9—H9A | 109.3 |

| | | | |
|---|---|---|---|
| C3—C2—C7 | 121.8 (2) | C10—C9—H9A | 109.3 |
| C3—C2—N1 | 131.8 (2) | N2—C9—H9B | 109.3 |
| C7—C2—N1 | 106.33 (19) | C10—C9—H9B | 109.3 |
| C4—C3—C2 | 116.0 (2) | H9A—C9—H9B | 107.9 |
| C4—C3—H3 | 122.0 | C9—C10—H10A | 109.5 |
| C2—C3—H3 | 122.0 | C9—C10—H10B | 109.5 |
| C3—C4—C5 | 122.2 (2) | H10A—C10—H10B | 109.5 |
| C3—C4—H4 | 118.9 | C9—C10—H10C | 109.5 |
| C5—C4—H4 | 118.9 | H10A—C10—H10C | 109.5 |
| C6—C5—C4 | 121.9 (2) | H10B—C10—H10C | 109.5 |
| C8—N1—C1—C1$^{i}$ | 93.4 (3) | C9—N2—C7—C6 | 4.6 (4) |
| C2—N1—C1—C1$^{i}$ | −90.1 (3) | C3—C2—C7—N2 | −178.0 (2) |
| C8—N1—C2—C3 | 177.2 (2) | N1—C2—C7—N2 | −0.8 (2) |
| C1—N1—C2—C3 | 0.2 (4) | C3—C2—C7—C6 | −1.4 (3) |
| C8—N1—C2—C7 | 0.4 (2) | N1—C2—C7—C6 | 175.8 (2) |
| C1—N1—C2—C7 | −176.6 (2) | C5—C6—C7—N2 | 176.3 (2) |
| C7—C2—C3—C4 | 1.1 (3) | C5—C6—C7—C2 | 0.7 (3) |
| N1—C2—C3—C4 | −175.2 (2) | C7—N2—C8—N1 | −0.7 (3) |
| C2—C3—C4—C5 | −0.3 (4) | C9—N2—C8—N1 | 179.5 (2) |
| C3—C4—C5—C6 | −0.4 (4) | C2—N1—C8—N2 | 0.2 (3) |
| C4—C5—C6—C7 | 0.2 (4) | C1—N1—C8—N2 | 177.24 (19) |
| C8—N2—C7—C2 | 1.0 (2) | C8—N2—C9—C10 | −109.6 (3) |
| C9—N2—C7—C2 | −179.2 (2) | C7—N2—C9—C10 | 70.6 (3) |
| C8—N2—C7—C6 | −175.2 (2) | | |

Symmetry codes: (i) −*x*+3/2, −*y*+3/2, −*z*+1.

**Fig. 1**


Br1A
C9
C10
N2
C8
N1
C1
C7
C2
C6
C5
C4
C3
O1
C4A
C3A
C5A
C2A
C6A
N1A
C7A
C1A
C8A
N2A
C10A
C9A
Br1
O1A