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5,6-Dioxo-1,10-phenanthrolin-1-ium bromide at 120 K

João A. S. Bomfim,[a] Carlos A. L. Filgueiras,[a] R. Alan Howie[b]* and James L. Wardell[a]

[a]Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: r.a.howie@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.029
wR factor = 0.077
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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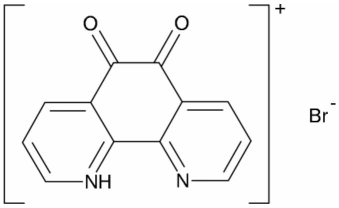
The title compound, $C_{12}H_7N_2O_2^+\cdot Br^-$ is, to our knowledge, the first reported example of a simple salt of cationic mono-*N*-protonated 1,10-phenanthroline-5,6-dione. All of the atoms lie on a crystallographic mirror plane and the cation is therefore totally planar. As a consequence, the compound has a well defined layer structure in which N—H···Br, C—H···Br and C—H···O contacts within the layers interconnect the ionic species.

Comment

A search of the current issue (Version 5.24) of the Cambridge Structural Database (Allen, 2002) reveals 144 structures containing the well known 1,10-phenanthroline ($C_{12}H_8N_2$, phen) moiety and a further 50 containing the related mono-*N*-protonated species ($C_{12}H_9N_2^+$, Hphen). In contrast, only three entries other than that corresponding to the ligand itself (MEJWED; Calderazzo *et al.*, 1999) are found for complexes containing the related 1,10-phenanthroline-5,6-dione ($C_{12}H_6N_2O_2$, pdon), and none at all for the corresponding N-protonated cation ($C_{12}H_7N_2O_2^+$, Hpdon). This is the basis for the claimed novelty of the structure of the compound described here, which is simply the Hpdon cation with a bromide counter-anion, *i.e* (Hpdon)Br, (I).



(I)

The asymmetric unit and atom-labelling scheme for (I) are shown in Fig. 1. All of the atoms lie on a crystallographic mirror plane. As a consequence, the cation, Hpdon, is completely planar. The comparatively high U_{eq} values of O1 and O2, ∼ $1.5U_{eq}$ of the other non-H atoms of the cation, suggests that the crystallographically induced planarity introduces a degree of simplification into the structural model because the planarity completely precludes displacement of O1 and O2 from the plane of the cation which might relieve any strain caused by intramolecular steric effects. However, the O1—C5—C6—O2 torsion angles of 3.4 (4) and −0.6 (4)° for the unconstrained unprotonated pdon molecules in Table 1 suggest that the displacement is likely to be small and the consequent degree of simplification negligible.

The remaining bond lengths and angles in Table 1 show that protonation to form the cation has no significant effect upon the bond lengths and that the only significant differences in

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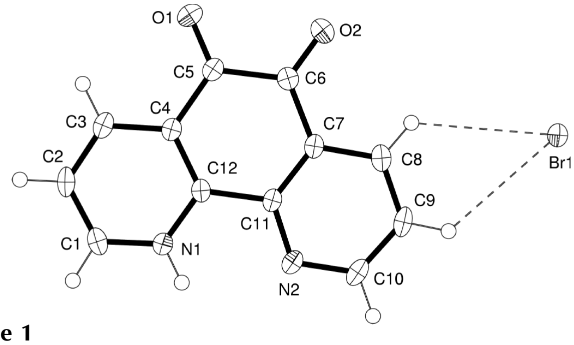

Figure 1

The asymmetric unit of (I), showing the labelling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as spheres of arbitrary radii. Dashed lines represent C—H···Br contacts (Table 2).

the geometries of Hpdon and pdon are the angles at protonated atom N1 and the adjacent atoms C1 and C12. Comparison of the molecular geometries of the analogous 1,10-phenanthroline species, phen (OPENAN; Nishigaki *et al.*, 1978) and (Hphen)Cl (CUZDIK; Hensen *et al.*, 2000), shows precisely the same effect, which is therefore presumed to be likely to occur in other *N*-aryl heterocyclic systems.

Because all of the atoms lie on crystallographic mirror planes of the space group *Pnma*, the constituent ions of (I) are found in well defined layers parallel to (010) (Fig. 2), $b/2$ [3.14890 (5) Å] apart. As shown in Fig. 2 and Table 2, a variety of N—H···Br, C—H···O and C—H···Br contacts occur within each layer. There are, however, no similar interlayer contacts. The layers, stacked in the direction of b, are related one to the next by the operation of crystallographic centres of symmetry (Fig. 3), in such a way that the cations overlap Br in adjacent layers but not, to any significant extent, one another. Thus, there is no π–π interaction between the layers, presumably because the interlayer separation (see above) is too small to accommodate it. Also discernible in Fig. 3 are channels parallel to b, centred on row vectors $\frac{1}{2},y,0$ and $0,y,\frac{1}{2}$, which, being unoccupied, account for the void space of 46.7 Å^3 per cell, ~4.2%, noted in the checkCIF report.

Experimental

The crystals of (I) were obtained as the result of the attempted recrystallization from moist, *i.e.* not specifically anhydrous, ethanol of the product obtained by reaction, over an extended period in ethanol solution, of dimethyltin dibromide and 1,10-phenanthroline-5,6-dione. The adventitious water has clearly brought about protonation of the intrinsically extremely basic dione ligand to provide the cation, and a degree of hydrolysis of the tin compound to provide the bromide counter-anion.

Crystal data

$C_{12}H_7N_2O_2^+\cdot Br^-$
$M_r = 291.11$
Orthorhombic, *Pnma*
$a = 14.2379\ (3)$ Å
$b = 6.2978\ (1)$ Å
$c = 12.3110\ (3)$ Å
$V = 1103.90\ (4)$ Å^3
$Z = 4$
$D_x = 1.752$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 10 916 reflections
$\theta = 2.9$–$27.5°$
$\mu = 3.71$ mm^{-1}
$T = 120\ (2)$ K
Block, orange
$0.30 \times 0.28 \times 0.08$ mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.248$, $T_{\max} = 0.283$
15 272 measured reflections

1376 independent reflections
1259 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 27.5°$
$h = -18 \rightarrow 18$
$k = -8 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 1.11$
1376 reflections
103 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.8806P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}

Table 1

Bond distances and angles (Å, °) in the Hpdon cation of (I) and molecular pdon.

	Hpdon[a]	pdon[b] Molecule 1	Molecule 2
C12—N1	1.344 (4)	1.343 (3)	1.339 (3)
N1—C1	1.337 (4)	1.336 (3)	1.336 (3)
C1—C2	1.376 (5)	1.379 (4)	1.369 (4)
C2—C3	1.386 (5)	1.370 (4)	1.371 (4)
C3—C4	1.397 (4)	1.391 (4)	1.385 (4)
C4—C5	1.493 (4)	1.476 (4)	1.477 (4)
C4—C12	1.386 (4)	1.395 (4)	1.402 (3)
C5—C6	1.542 (4)	1.529 (4)	1.539 (4)
C5—O1	1.208 (4)	1.214 (3)	1.207 (3)
C6—C7	1.485 (4)	1.476 (4)	1.469 (4)
C6—O2	1.205 (4)	1.208 (3)	1.209 (3)
C7—C8	1.392 (4)	1.391 (4)	1.389 (4)
C7—C11	1.397 (4)	1.401 (3)	1.393 (4)
C8—C9	1.381 (5)	1.371 (4)	1.365 (4)
C9—C10	1.392 (5)	1.369 (4)	1.376 (4)
C10—N2	1.345 (4)	1.339 (3)	1.338 (3)
N2—C11	1.334 (4)	1.339 (3)	1.343 (3)
C11—C12	1.473 (4)	1.489 (4)	1.494 (3)
C12—N1—C1[c]	123.2 (3)	116.7 (2)	116.7 (2)
N1—C1—C2[c]	120.1 (3)	125.0 (2)	125.2 (3)
C1—C2—C3	118.9 (3)	118.0 (3)	117.9 (3)
C2—C3—C4	119.8 (3)	118.8 (3)	119.3 (2)
C3—C4—C5	121.1 (3)	123.1 (3)	120.2 (2)
C3—C4—C12	119.2 (3)	119.2 (2)	118.6 (2)
C5—C4—C12	119.6 (3)	120.8 (2)	121.2 (2)
C4—C5—C6	117.7 (2)	118.1 (2)	117.9 (2)
C4—C5—O1	122.2 (3)	123.1 (3)	123.0 (2)
C6—C5—O1	120.1 (3)	118.8 (2)	119.1 (2)
C5—C6—C7	118.2 (2)	118.2 (2)	117.9 (2)
C5—C6—O2	119.0 (3)	119.5 (2)	118.9 (2)
C7—C6—O2	122.8 (3)	122.3 (2)	123.3 (3)
C6—C7—C8	121.1 (3)	120.0 (2)	119.4 (2)
C6—C7—C11	121.0 (3)	121.0 (2)	121.8 (2)
C8—C7—C11	117.9 (3)	119.0 (2)	118.9 (2)
C7—C8—C9	118.8 (3)	118.6 (2)	119.3 (3)
C8—C9—C10	119.0 (3)	118.5 (3)	118.3 (3)
C9—C10—N2	123.3 (3)	124.7 (3)	124.2 (2)
C10—N2—C11	116.8 (3)	117.0 (2)	117.3 (2)
N2—C11—C12	115.8 (2)	117.4 (2)	117.3 (2)
N2—C11—C7	124.2 (3)	122.1 (2)	122.1 (2)
C12—C11—C7	120.0 (3)	120.6 (2)	120.6 (2)
C11—C12—N1	117.8 (2)	116.6 (2)	117.0 (2)
C11—C12—C4	123.5 (3)	121.2 (2)	120.6 (2)
N1—C12—C4[c]	118.8 (3)	122.2 (2)	122.4 (2)
O1—C5—C6—O2	0	3.4 (4)	−0.6 (4)

Notes: (*a*) atom designations as for Hpdon in Fig. 1; (*b*) values obtained with *PLATON* (Spek, 1990) from CSD CIF data (MEJWED; Calderazzo *et al.*, 1999); (*c*) entries showing particularly marked differences between Hpdon and pdon.

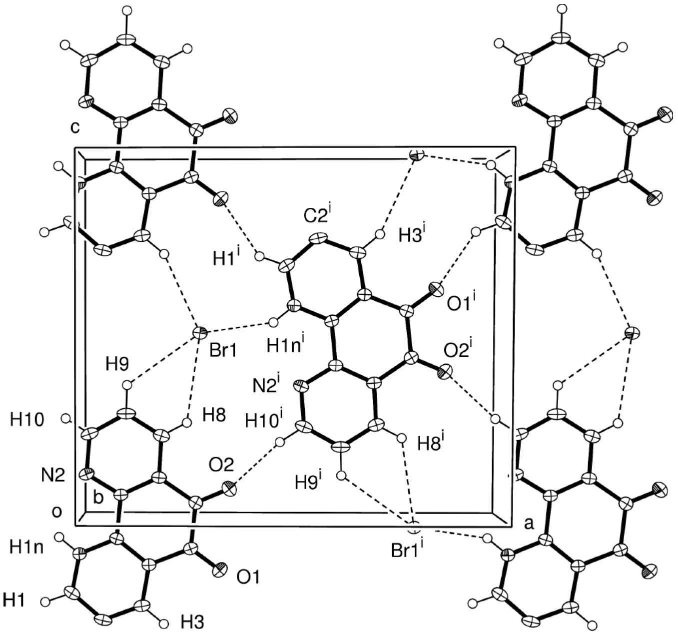

Figure 2
A portion of a single layer in the structure of (I), viewed along *b*. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms participating in $X-\text{H}\cdots Y$ (X = N or C; Y = Br or O) contacts (dashed lines, Table 2) as spheres of arbitrary radius. Selected atoms are labelled. [Symmetry code: (i) $\frac{1}{2}+x, y, \frac{1}{2}-z$.]

Table 2
Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N}\cdots\text{Br1}^{i}$	0.88	2.45	3.239 (2)	149
$\text{C1}-\text{H1}\cdots\text{O1}^{ii}$	0.95	2.29	3.102 (4)	143
$\text{C3}-\text{H3}\cdots\text{Br1}^{iii}$	0.95	2.87	3.748 (3)	154
$\text{C10}-\text{H10}\cdots\text{O2}^{i}$	0.95	2.29	3.227 (4)	170
$\text{C8}-\text{H8}\cdots\text{Br1}$	0.95	3.00	3.640 (3)	126
$\text{C9}-\text{H9}\cdots\text{Br1}$	0.95	2.97	3.625 (3)	127

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

All H atoms were placed in calculated positions, with C—H and N—H distances of 0.95 and 0.88 Å, respectively, and were refined with a riding model, with $U_{\rm iso}$ values equal to $1.2U_{\rm eq}$ of the non-H atom to which they are attached.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1990).

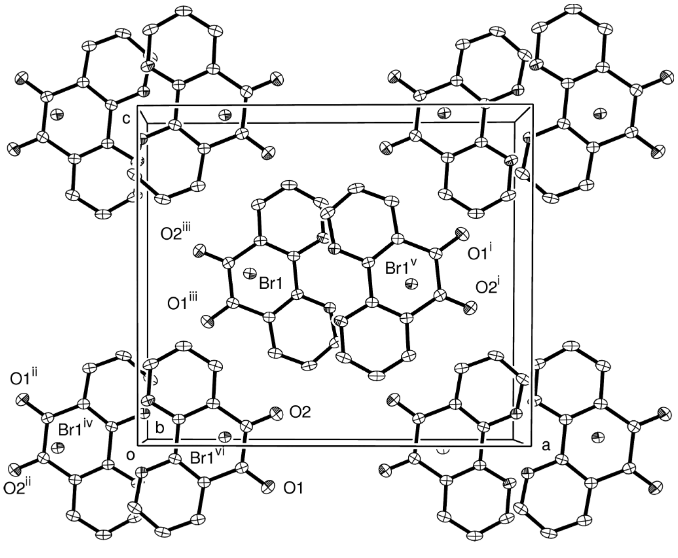

Figure 3
The cell contents of (I), viewed along *b*. The representation is the same as in Fig. 2, except that H atoms and the $X-\text{H}\cdots Y$ contacts have been omitted for clarity. [Symmetry codes: (i) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (ii) $-x, 1-y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iv) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (v) $1-x, 1-y, 1-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$.]

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