organic papers

2-Bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dionate bromide

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At 150 K, the title compound, $C_{11}H_{18}BrN_2O_2{}^+\cdot Br^-$, is a salt comprising monoprotonated 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dione cations and bromide anions. In the cation, the acidic proton is intramolecularly hydrogen-bonded between the carbonyl O atoms and the positive charge is delocalized over both amide groups.

Comment

The title compound, (I), crystallizes as a salt comprising monoprotonated 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dione cations and bromide anions (Fig. 1). In the cation, the location of the acidic proton, H1, between the carbonyl O atoms was identified in a difference Fourier map, which also indicated that H1 formed a non-symmetrical hydrogen bond disordered over the two equivalent positions dictated by the crystallographic mirror symmetry. This description was confirmed by the successful free refinement of the positional parameters of H1 to give a satisfactory hydrogen-bond geometry (Table 3). The delocalization of the positive charge over the amide groups is confirmed by the long C=O distance of 1.281 (5) Å and the short C—N distance of 1.301 (5) Å.


(I)
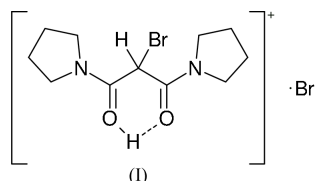
The interatomic contact distances for the bromide anion Br2 (Table 2) show that the shortest inter-ion interactions are within a one-dimensional alternating sequence of cations and anions parallel to the crystallographic c axis (Fig. 2). The short Br2$\cdots$Br1[ii] [symmetry code: (ii) x, y, $1 + z$] distance of 3.1049 (8) Å is associated with a long C1—Br1 distance of 2.001 (7) Å, and both of these features are consistent with a weak C1—Br1 bond and some cationic character for Br1. The close contacts between Br2 and C1, C2 and H1A rather than H1 also indicate that the charge on the cation is associated with the central C atoms of the diamide moiety rather than the formal site of protonation.

Experimental

The title compound, (I), was prepared by the reaction of 1,3-dipyrrolidin-1-ylpropane-1,3-dione (Wilson & Weingarten, 1970) with bromine in dichloromethane at room temperature, according to the method of Malmberg *et al.* (1983). Suitable crystals were grown by recrystallization from dichloromethane. Spectroscopic analysis, ^{1}H NMR (CDCl$_3$, δ): 16.05 (*br s*, 1H, OH), 5.88 (*s*, 1H, CH), 3.96 (*br s*, 4H), 3.67 (*t*, 4H), 2.14 (*m*, 4H), 2.03 (*m*, 4H); MS (EI, *m/z*): 289;
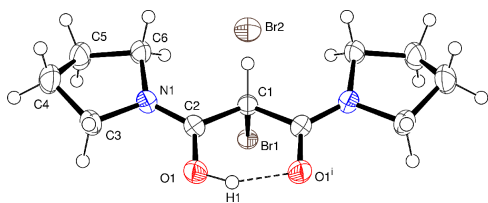
Figure 1
View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitary size. The symmetry code is as in Table 1.
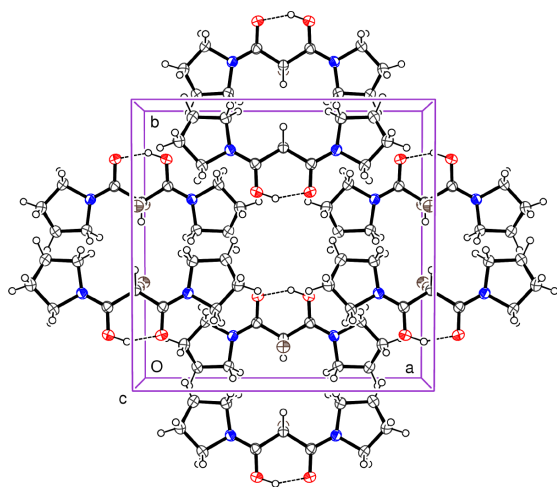
Figure 2
The packing of (I), viewed down the crystallographic c axis. For clarity, only one of the two equivalent sites for the intramolecularly hydrogen-bonded atom H1 is shown.

analysis calculated for $C_{11}H_{18}Br_2N_2O_2$: C 35.70, H 4.90, N 7.57%; found: C 35.67, H 4.95, N 7.37%.

Crystal data

$C_{11}H_{18}BrN_2O_2^+ \cdot Br^-$	Mo $K\alpha$ radiation
$M_r = 370.09$	Cell parameters from 7940
Orthorhombic, $Cmc2_1$	reflections
$a = 13.4235\ (13)$ Å	$\theta = 3.0–34.8°$
$b = 12.9358\ (10)$ Å	$\mu = 5.62\ mm^{-1}$
$c = 8.2935\ (6)$ Å	$T = 150\ (2)$ K
$V = 1440.1\ (2)$ Å^3	Needle, pale yellow
$Z = 4$	$0.50 \times 0.20 \times 0.15$ mm
$D_x = 1.707$ Mg m^{-3}	

Data collection

Stoe IPDS-II area-detector	3007 independent reflections
diffractometer	2578 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.039$
Absorption correction: numerical	$\theta_{max} = 34.8°$
(X-$SHAPE$; Stoe & Cie, 2001)	$h = -21 \rightarrow 21$
$T_{min} = 0.263$, $T_{max} = 0.502$	$k = -20 \rightarrow 20$
10 894 measured reflections	$l = -13 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 7.6558P]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
3007 reflections	$\Delta\rho_{max} = 1.25$ e Å^{-3}
87 parameters	$\Delta\rho_{min} = -0.96$ e Å^{-3}
H atoms treated by a mixture of	Extinction correction: $SHELXL$97
independent and constrained	Extinction coefficient: 0.0136 (9)
refinement	Absolute structure: Flack (1983),
	1313 Friedel pairs
	Flack parameter = 0.01 (2)

Table 1
Selected geometric parameters (Å, °).

Br1—C1	2.001 (7)	C1—C2	1.513 (6)
O1—C2	1.281 (5)	C3—C4	1.511 (7)
N1—C2	1.301 (5)	C4—C5	1.515 (9)
N1—C6	1.480 (6)	C5—C6	1.526 (7)
N1—C3	1.483 (6)		
C2—O1—H1	112 (6)	C2—C1—Br1	105.6 (3)
C2—N1—C6	126.1 (4)	O1—C2—N1	120.3 (4)
C2—N1—C3	121.9 (4)	O1—C2—C1	119.7 (4)
C6—N1—C3	112.0 (3)	N1—C2—C1	119.8 (4)
C2—C1—C2^i	112.1 (5)		
C6—N1—C2—O1	−179.7 (5)	C2^i—C1—C2—O1	−21.3 (8)
C3—N1—C2—O1	1.6 (7)	Br1—C1—C2—O1	93.2 (5)
C6—N1—C2—C1	−4.4 (7)	C2^i—C1—C2—N1	163.4 (3)
C3—N1—C2—C1	176.9 (5)	Br1—C1—C2—N1	−82.2 (5)

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

Table 2
Contact disctances (Å).

Br2···Br1^{ii}	3.1049 (8)	Br2···H1A	2.884
Br2···C1	3.201 (7)	Br2···H6A^{iii}	3.027
Br2···C2	3.234 (4)	Br2···H6B	3.586
Br2···O1	3.663 (4)	Br2···H1	3.63 (12)
Br2···N1	3.677 (4)		

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

Table 3
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O1^i	0.89 (10)	1.59 (10)	2.405 (4)	149 (10)

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

All H atoms were initially located in a difference Fourier map. The 0.5-occupancy hydroxyl H-atom positional parameters were refined freely, along with an isotropic displacement parameter. All other H atoms were placed in geometrically idealized positions with C—H distances of 0.99–1.00 Å and U_{iso}(H) values set at $1.2U_{eq}$(C). The largest density peak in the final difference Fourier map is 1.08 Å from Br2 and is the only residual peak greater than 1 e Å^{-3}.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-RED*32 (Stoe & Cie, 2001); data reduction: *X-RED*32; program(s) used to solve structure: *X-STEP*32 (Stoe & Cie, 2001) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for *Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX*.

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