

## Secondary interactions in 3-bromopyridinium tribromoacetate

Peter G. Jones\* and Virginia Lozano

Institut für Anorganische und Analytische Chemie, Technische Universität  
Braunschweig, Postfach 3329, 38023 Braunschweig, Germany  
Correspondence e-mail: p.jones@tu-bs.de

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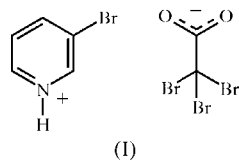
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The title compound,  $C_5H_5BrN^+ \cdot C_2Br_3O_2^-$ , crystallizes with  $Z' = 2$ . The residues pack in two distinct (but interconnected) types of layer, namely, layers parallel to (102), in which the residues are connected by classical  $N-H \cdots O$  hydrogen bonds,  $C-H \cdots O$  interactions and  $Br \cdots Br$  contacts, and anion layers parallel to the  $ab$  plane, connected by  $Br \cdots O$  interactions. The two formula units are topologically equivalent with respect to all these contacts.

## Comment

We are interested in secondary bonding contacts (classical and 'weak' hydrogen bonds, and halogen-halogen contacts) in structures of pyridine derivatives, such as 4-iodopyridine (Ahrens & Jones, 1999), hydroxypyridines and pyridones (Jones, 2001; Flakus *et al.*, 2003), pyridinethiones (Flakus *et al.*, 2001), halopyridinium halides (Freytag *et al.*, 1999; Freytag & Jones, 2001; Jones & Lozano, 2003a) and halomethylpyridinium halides (Jones *et al.*, 2002; Jones & Vancea, 2003; Lozano & Jones, 2004). We considered it worthwhile to extend our studies using halogen-rich anions rather than simple halides, and report here the structure of 3-bromopyridinium tribromoacetate, (I). This is the first structure involving a free tribromoacetate ion; a search of the Cambridge Database (CSD, Version of July 2004; Allen, 2002) revealed one structure with a tribromoacetate ligand in a copper(II) complex (refcode CIYFUL; Porter & Doedens, 1984).



The asymmetric unit of (I) contains two formula units (Fig. 1), both consisting of a cation-anion pair linked by a classical  $N-H \cdots O$  hydrogen bond. Atom labels of the second formula unit are distinguished by an additional initial digit 1. Bond lengths and angles may be considered normal, e.g. the somewhat widened ring angles at N, or the  $C-Br$  bond

lengths of the anion, which are closely similar to those of the free acid (Jones & Lozano, 2003b). The  $C-O$  bond lengths differ significantly, those involving hydrogen-bonded atoms O1 and O11 being longer (Table 1). Both anions adopt a conformation in which one Br atom (Br2 or Br12) lies in the carboxylate plane, with  $Br-C-C-O$  torsion angles of 2.3 (4) and  $-1.7$  (4)° [*cf.*  $-16.4$  (3)° in the free acid; Jones & Lozano, 2003b].

The crystal packing of (I) appears at first sight to be a complex three-dimensional network, but can be analysed in terms of two (interconnected) layer structures associated with different types of non-bonded contacts. The first such layer type (Fig. 2), parallel to (102), involves the classical hydrogen bonds, two very short  $C-H \cdots O$  interactions (normalized  $H \cdots O$  distances of 2.27 and 2.31 Å) from the H atoms at C6 and C16 (Table 2), and the four shortest  $Br \cdots Br$  contacts (Table 3). Carboxylate atoms O1 and O11 represent bifur-

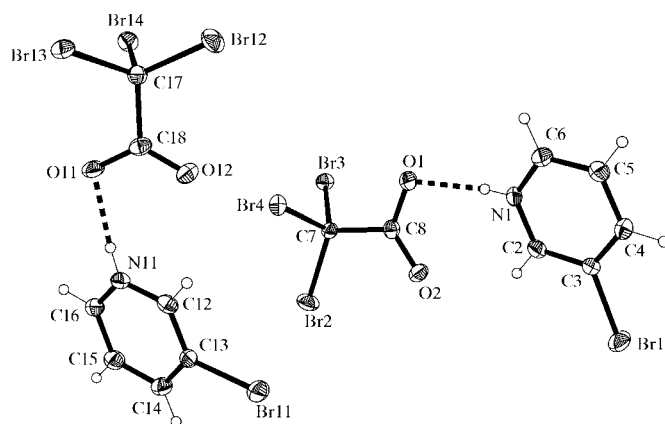


Figure 1

The formula unit of (I) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds.

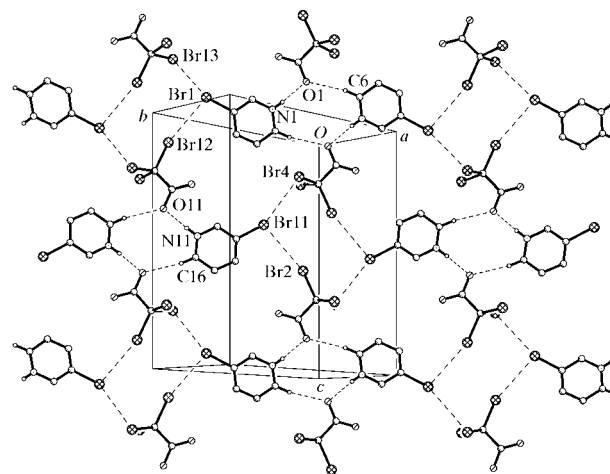


Figure 2

A packing diagram for (I), illustrating the layer structure formed *via* classical hydrogen bonds,  $C-H \cdots O$  interactions and  $Br \cdots Br$  contacts (all shown as dashed lines), viewed perpendicular to (102). H atoms not involved in hydrogen bonds have been omitted for clarity. Atom Br2 is at the symmetry position  $(1-x, 1-y, 1-z)$ , Br4 and C6 are at  $(1+x, y, z)$ , Br1, N1 and O1 are at  $(1-x, 1-y, -z)$ , and Br13 is at  $(-x, 2-y, -z)$ . Other labelled atoms are those of the asymmetric unit.

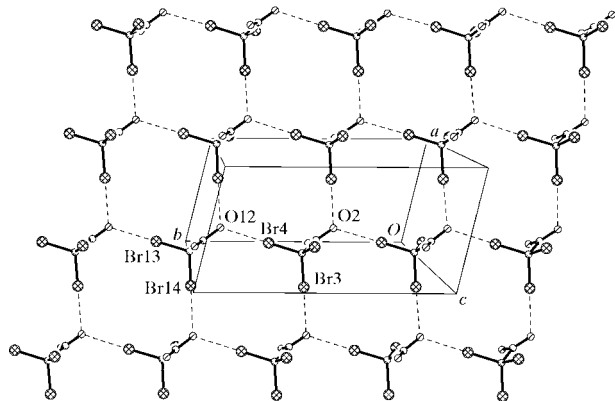
cated systems, each accepting one N—H···O and one C—H···O hydrogen bond. The hydrogen bonds of each of the two formula units combine to form independent centrosymmetric rings of graph set  $R_4^2(10)$ . (Bernstein *et al.*, 1995).

Each cation Br atom (Br1 or Br11) is involved in two Br···Br contacts, to an anion Br atom of two different anions of the other respective formula unit (Br12 and Br13, and Br2 and Br4). This results in two independent eight-membered rings. The ten- and eight-membered rings alternate to connect cations, forming chains in the direction  $[2\bar{1}0]$  (horizontal in Fig. 2), whereby each cation has its own independent chain. The two independent anions alternate in the same direction.

All four Br···Br contacts correspond approximately to 'type II', according to the classification of Pedireddi *et al.* (1994), with one C—Br···Br angle of *ca* 180° and one of *ca* 90°. This is consistent with the concept of a region of positive charge in the extension of the C—Br vector beyond the Br atom, which interacts with the negative region perpendicular to the C—Br bond of the second Br atom. The Br atoms in the cations would be expected to have enhanced positive charge regions and thus preferentially form linear contacts, but, clearly, only one contact from Br1 or Br11 can be linear at these atoms, and the respective second contacts are therefore linear at Br12 and Br2.

The second layer type in the structure of (I) is associated with Br···O contacts. These may be regarded as a type of 'halogen bond' (Metrangolo & Resnati, 2001). We had expected these to be formed between cations and anions (charge-assisted contacts) but were surprised to observe, despite the unfavourable electrostatic effects, that the anions associate amongst themselves. We have, however, frequently observed a similar effect with C—H···O contacts between di(methanesulfonyl)amide anions (*e.g.* Moers, Lange *et al.*, 2001; Moers, Wijaya *et al.*, 2001; Henschel *et al.*, 2002).

The independent anions alternate in chains parallel to the *b* axis, and these chains are linked by translation along *a* to form a layer, consisting of two independent but topologically identical types of 12-membered ring parallel to the *ab* plane



**Figure 3**

A packing diagram for (I), illustrating the tribromoacetate network at  $c \simeq \frac{1}{4}$ , viewed perpendicular to the *ab* plane. Dashed lines indicate Br···O interactions. All labelled atoms are those of the reference asymmetric unit.

(Fig. 3). The four independent contacts (Table 3) involve those Br atoms not coplanar with the carboxylate groups (Br3, Br4, Br13 and Br14), together with the O atoms not involved in hydrogen bonds (O2 and O12, both double acceptors), and are all short: *cf.* 3.009 (2) Å in tribromoacetic acid (Jones & Lozano, 2003*b*), 2.974 (4) Å in sodium bromate (Abrahams & Bernstein, 1977), or 3.197 (3)–3.338 (4) Å in two modifications of di(4-bromobenzenesulfonyl)amine (Lozano *et al.*, 2004). All C—Br···O angles are, as expected (Lommerse *et al.*, 1996), approximately linear. For Br4 and Br13, this complements their perpendicular Br···Br—C angles, whereas Br2 and Br12 (and of course Br1 and Br11 of the cations) have already 'used up' their linear contacts in the Br···Br interactions (see above) and thus are no longer available for Br···O contacts. The Br···O—C angles are close to the expected values of 120°, corresponding to the lone-pair directions, but this is not always the case, as pointed out by Lommerse *et al.* (1996).

There are also two approximately linear C—H···Br contacts that might be regarded as weak hydrogen bonds. These connect neighbouring layers parallel to (102), but we attribute to them a subordinate role in determining the packing. Two further such contacts, but with very narrow angles, are included in Table 2 for completeness.

There is considerable current interest in structures with  $Z' > 1$ , in view of their implications for crystal engineering (see, for example, Steed, 2003). We note that, neglecting the C—H···Br interactions, the two formula units of (I) are exactly equivalent in their topology; each secondary contact finds a topological counterpart on exchanging the atoms of the two formula units. Thus, there is no obvious explanation for the  $Z'$  value of 2.

## Experimental

A solution of 3-bromopyridine (0.24 ml, 2.5 mmol) and tribromoacetic acid (0.742 g, 2.5 mmol) in dichloromethane (10 ml) was stirred for 1 h and the product, (I), was precipitated by adding petroleum ether (b.p. 313–333 K) (yield 0.523 g, 46%). Single crystals were obtained by diffusion of petroleum ether (b.p. 313–333 K) into a dichloromethane solution of (I).

### Crystal data

$C_5H_5BrN^+ \cdot C_2Br_3O_2^-$   
 $M_r = 454.76$   
 Triclinic,  $P\bar{1}$   
 $a = 6.2478$  (4) Å  
 $b = 12.6754$  (8) Å  
 $c = 15.4525$  (8) Å  
 $\alpha = 96.520$  (4)°  
 $\beta = 95.900$  (4)°  
 $\gamma = 103.883$  (4)°  
 $V = 1169.53$  (12) Å<sup>3</sup>

$Z = 4$   
 $D_x = 2.583$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 7447 reflections  
 $\theta = 2.3$ – $30.5$ °  
 $\mu = 13.74$  mm<sup>-1</sup>  
 $T = 133$  (2) K  
 Tablet, colourless  
 $0.16 \times 0.13 \times 0.07$  mm

### Data collection

Bruker SMART1000 CCD area-detector diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{min} = 0.168$ ,  $T_{max} = 0.382$   
 22 507 measured reflections

6811 independent reflections  
 5031 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.041$   
 $\theta_{max} = 30.0$ °  
 $h = -8 \rightarrow 8$   
 $k = -17 \rightarrow 17$   
 $l = -21 \rightarrow 21$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.056$   
 $S = 0.92$   
 6811 reflections  
 261 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0219P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.74 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.92 \text{ e } \text{Å}^{-3}$

**Table 1**  
 Selected geometric parameters (Å, °).

|              |           |                  |           |
|--------------|-----------|------------------|-----------|
| C7—Br2       | 1.931 (3) | C17—Br12         | 1.937 (3) |
| C7—Br3       | 1.942 (3) | C17—Br13         | 1.944 (3) |
| C7—Br4       | 1.941 (3) | C17—Br14         | 1.943 (3) |
| C8—O1        | 1.265 (4) | C18—O11          | 1.270 (4) |
| C8—O2        | 1.225 (4) | C18—O12          | 1.221 (3) |
| C6—N1—C2     | 122.8 (3) | C16—N11—C12      | 122.8 (3) |
| Br2—C7—C8—O2 | 2.3 (4)   | Br12—C17—C18—O12 | −1.7 (4)  |

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

| $D-H\cdots A$                       | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|----------|-------------|-------------|---------------|
| N1—H01 $\cdots$ O1                  | 0.75 (3) | 1.89 (4)    | 2.632 (3)   | 172 (4)       |
| N11—H011 $\cdots$ O11               | 0.80 (4) | 1.82 (4)    | 2.621 (4)   | 175 (4)       |
| C6—H6 $\cdots$ O1 <sup>i</sup>      | 0.95     | 2.40        | 3.334 (4)   | 168           |
| C16—H16 $\cdots$ O11 <sup>ii</sup>  | 0.95     | 2.44        | 3.373 (4)   | 169           |
| C2—H2 $\cdots$ Br13 <sup>iii</sup>  | 0.95     | 3.05        | 3.939 (3)   | 157           |
| C12—H12 $\cdots$ Br14 <sup>iv</sup> | 0.95     | 3.08        | 3.997 (3)   | 163           |
| C16—H16 $\cdots$ Br14 <sup>ii</sup> | 0.95     | 3.12        | 3.626 (3)   | 115           |
| C5—H5 $\cdots$ Br3 <sup>i</sup>     | 0.95     | 3.08        | 3.748 (3)   | 129           |

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

**Table 3**  
 Br $\cdots$ Br and Br $\cdots$ O contacts for (I) (Å, °).

| $C-Br\cdots X-C$  | $Br\cdots X$ | $C-Br\cdots X$ | $Br\cdots X-C$ |
|---|--------------|----------------|----------------|
| C3—Br1 $\cdots$ Br12 <sup>v</sup> —C17 <sup>v</sup>     | 3.5778 (5)   | 102.52 (9)     | 159.82 (9)     |
| C13—Br11 $\cdots$ Br2 <sup>vi</sup> —C7 <sup>vi</sup>   | 3.6935 (5)   | 101.64 (10)    | 158.19 (9)     |
| C3—Br1 $\cdots$ Br13 <sup>vii</sup> —C17 <sup>vii</sup> | 3.6359 (5)   | 146.18 (10)    | 92.73 (9)      |
| C13—Br11 $\cdots$ Br4 <sup>iv</sup> —C7 <sup>iv</sup>   | 3.7098 (5)   | 152.47 (10)    | 87.52 (8)      |
| C13—Br11 $\cdots$ Br3 <sup>iv</sup> —C7 <sup>iv</sup>   | 3.8880 (5)   | 136.98 (9)     | 82.47 (9)      |
| C7—Br2 $\cdots$ Br2 <sup>viii</sup> —C7 <sup>viii</sup> | 3.9196 (7)   | 128.26 (8)     | 128.26 (8)     |
| C7—Br3 $\cdots$ O2 <sup>ix</sup> —C8 <sup>ix</sup>      | 2.808 (2)    | 177.49 (10)    | 123.5 (2)      |
| C7—Br4 $\cdots$ O12—C18                                 | 2.833 (2)    | 174.90 (10)    | 124.5 (2)      |
| C17—Br13 $\cdots$ O2 <sup>x</sup> —C8 <sup>x</sup>      | 2.848 (2)    | 167.68 (10)    | 129.2 (2)      |
| C17—Br14 $\cdots$ O12 <sup>ix</sup> —C18 <sup>ix</sup>  | 2.849 (2)    | 171.23 (10)    | 125.3 (2)      |

Symmetry codes: (iv)  $1 + x, y, z$ ; (v)  $1 - x, 1 - y, -z$ ; (vi)  $1 - x, 1 - y, 1 - z$ ; (vii)  $1 + x, y - 1, z$ ; (viii)  $-x, 1 - y, 1 - z$ ; (ix)  $x - 1, y, z$ ; (x)  $x, 1 + y, z$ .

H atoms bonded to nitrogen were refined freely. Other H atoms were included using a riding model, with C—H distances of 0.95 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1583). Services for accessing these data are described at the back of the journal.

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