Tribromoacetic acid

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Key indicators

Single-crystal X-ray study

$T = 133$ K

Mean σ(C–C) = 0.003 Å

R factor = 0.022

wR factor = 0.053

Data-to-parameter ratio = 26.8

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

The packing of the title compound, $C_2HBr_3O_2$, involves regions of hydrogen-bonded carboxylic acid dimers, in turn linked by two contacts of the type Br···Br and one Br···O.

Comment

We have begun to investigate the structures of tribromo-acetates and therefore decided to determine the structure of the parent acid, tribromoacetic acid. The structure of trichloroacetic acid has recently been reported by Rajagopal *et al.* (2003).

(I)
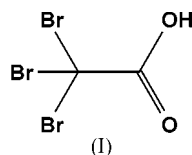
The molecular structure of tribromoacetic acid, (I), is presented in Fig. 1. Bond lengths and angles may be regarded as normal, in particular the C—O bond lengths, which show no signs of the disorder sometimes observed in carboxylic acids (for a detailed discussion, see Wilson, 2002). Atom Br2 is approximately synperiplanar to O1.

More interesting features are observed in the packing. Apart from the classical 'carboxylic acid dimer' formed by hydrogen bonding, there are three significant contacts involving atom Br1; 3.6284 (5) Å to $Br2(x - \frac{1}{2}, y - \frac{1}{2}, z)$, 3.6193 (5) Å to $Br3(-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$, and 3.009 (2) Å to the carbonyl atom $O2(x - \frac{1}{2}, y + \frac{1}{2}, z)$.

The Br···Br contacts are established as 'type II' in the classification of Pedireddi *et al.* (1994) by the angles at bromine; 101.25 (7)/167.92 (7)° for the first and 93.77 (7)/167.05 (7)° for the second. Such contacts are thought to be associated with a positive region of charge in the extension of the C—Br vector beyond Br, which can interact with the negative region perpendicular to the C—Br bond at the other bromine. The somewhat longer Br3···Br3 interaction of 3.8020 (5) Å (code: $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$), however, has equal angles at bromine [142.57 (7)°, equal by symmetry] and such 'type I' contacts are regarded as less energetically favourable.

Contacts of the type Br···O may be regarded as one form of 'halogen bond' (Metrangolo & Resnati, 2001). Although the distance observed here is significantly shorter than the sum of the van der Waals radii (Br = 1.85 Å and O = 1.52 Å; Bondi, 1964), much shorter values have been observed (down to *ca* 2.7 Å, as quoted in the above-mentioned article). Lommerse *et al.* (1996), in a review of contacts between halogens and oxygen or nitrogen, pointed out that these also tend to be
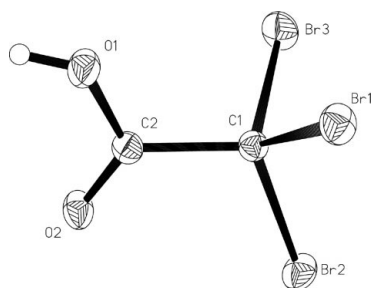
DOI: 10.1107/S1600536803007268

Figure 1
The molecule of the title compound in the crystal. Ellipsoids are drawn at the 50% probability level. The H atom radius is arbitrary.

Figure 2
Packing diagram of the title compound viewed perpendicular to the *ab* plane. Secondary interactions are indicated by dashed lines.
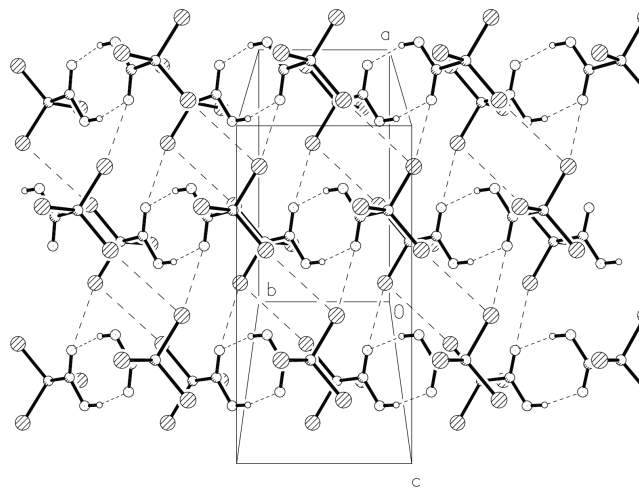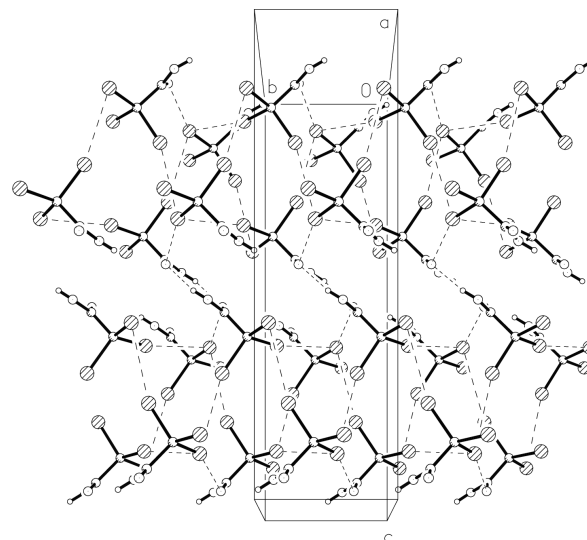

Figure 3
Packing diagram of the title compound viewed perpendicular to the *bc* plane. Secondary interactions are indicated by dashed lines.

approximately linear at the halogen [here 157.24 (8)°], but show little preferred directionality to the O-atom lone pairs [here the bromine lies 1.964 (5) Å out of the C1/C2/O1/O2 plane]. Again, electrostatic forces are thought to play an important role.

The net effect of the contacts can be seen in the packing diagrams. Carboxylic acid dimers occupy the regions $z \simeq 0, \frac{1}{2}$, 1, *etc.* Fig. 2 shows the region at $z \simeq \frac{1}{2}$, with dimer formation supported by Br1···Br2 and Br1···O2; Br1···Br3 links the CBr_3 moieties of successive dimer regions to form double layers of molecules between *e.g.* $z \simeq \frac{1}{2}$ and 1 (Fig. 3).

Experimental

The title material was purchased from Aldrich. Single crystals grew from a solution in dichloromethane/petrol ether (*ca* 1/5 *v/v*) on cooling to 255 K.

Crystal data

$C_2HBr_3O_2$	$D_x = 3.155$ Mg m^{-3}
$M_r = 296.76$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4624
$a = 11.1679$ (12) Å	reflections
$b = 5.7966$ (6) Å	$\theta = 3.8–30.5°$
$c = 19.821$ (2) Å	$\mu = 19.26$ mm^{-1}
$\beta = 103.132$ (4)°	$T = 133$ (2) K
$V = 1249.6$ (2) Å^3	Tablet, colourless
$Z = 8$	$0.15 \times 0.13 \times 0.04$ mm

Data collection

Bruker SMART 1000CCD diffractometer	1823 independent reflections
	1577 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.037$
Absorption correction: multi-scan	$\theta_{max} = 30.0°$
(*SADABS*; Bruker, 1998)	$h = -15 \rightarrow 15$
$T_{min} = 0.268, T_{max} = 0.564$	$k = -8 \rightarrow 8$
9331 measured reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$
$wR(F^2) = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
1823 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
68 parameters	$\Delta\rho_{min} = -0.80$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.934 (2)	O1—C2	1.302 (3)
Br2—C1	1.929 (3)	O2—C2	1.219 (3)
Br3—C1	1.944 (2)	C1—C2	1.539 (3)
C2—C1—Br2	110.56 (17)	Br1—C1—Br3	109.90 (12)
C2—C1—Br1	111.01 (17)	O2—C2—O1	126.2 (2)
Br2—C1—Br1	109.85 (12)	O2—C2—C1	121.0 (2)
C2—C1—Br3	105.38 (16)	O1—C2—C1	112.7 (2)
Br2—C1—Br3	110.08 (12)		
Br2—C1—C2—O2	−16.4 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H01···O2^i	0.76 (4)	1.95 (4)	2.691 (3)	162 (4)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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