organic papers

Ji-Xin Yuan

School of Chemistry and Materials Science,
Wenzhou University, Wenzhou 325027,
People's Republic of China

Correspondence e-mail:
zkrist2005@yahoo.com.cn

Key indicators

Single-crystal X-ray study
$T = 298$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.055
wR factor = 0.123
Data-to-parameter ratio = 13.1

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

2,2′-Biimidazol-1-ium trichloroacetate

The 2,2′-biimidazol-1-ium trichloroacetate ion pairs in the title compound, $C_6H_7N_4^+ \cdot C_2Cl_3O_2^-$, are held together by two N—H$\cdots$O hydrogen bonds, and two adjacent ion pairs are linked into a centrosymmetric dimer by a pair of N—H$\cdots$N hydrogen bonds. The hydrogen-bonding pattern can be described in graph-set motif notation as $R_2^2(9)$ and $R_2^2(10)$. Moreover, the adjacent dimers are associated by π–π interactions between five-membered rings of the 2,2′-biimidazol-1-ium cations [at (x, y, z) and $(2 - x, -y, 1 - z)$], with the ring centroids separated by 3.861 (1) Å, forming a ribbon-like supramolecular array along the b axis.

Comment

2,2′-Biimidazole, H_2biim, is not only a proton donor, but also a proton acceptor, so that it possesses five possible forms, *viz.* di-deprotonated (dianion, $biim^{2-}$), mono-deprotonated (mono-anion, $Hbiim^-$), neutral (neutral, H_2biim), mono-protonated (monocation, H_3biim^+) and di-protonated (dication, H_4biim^{2+}). Therefore, H_2biim is an excellent candidate for the development of supramolecular motifs in crystal structures. Homomeric hydrogen-bonded motifs $R_2^2(10)$ (Cromer *et al.*, 1987), heteromeric hydrogen-bonded motifs $R_2^2(9)$ (Ye *et al.*, 2005) and $R_2^1(7)$ (Bélanger & Beauchamp, 1996), and mixed hydrogen-bonded motifs $R_2^2(10)$ and $R_2^1(7)$ (Ramirez *et al.*, 2002), have been structurally reported. In an extension of this research, the crystal structure of the title compound, $C_6H_7N_4^+ \cdot C_2Cl_3O_2^-$, (I), is reported here.

(I)
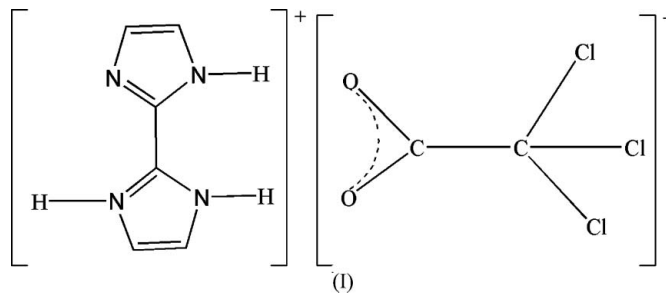
The bond distances and angles of the mono-protonated H_3biim^+ in (I) are unexceptional and compare well with the values in neutral H_2biim (Cromer *et al.*, 1987) (Table 1 and Fig. 1). The two rings are almost coplanar in both cases. The dihedral angle between the two five-membered rings in neutral H_2biim is 4.6°, and is slightly smaller in (I) at 4.47 (3)°.

Two N—H$\cdots$O hydrogen bonds connect the H_3biim^+ cations and trichloroacetate anions to produce ion pairs, and two adjacent ion pairs are linked into a dimer by a third N3—H3$A\cdots$N2^i hydrogen bond and its inversion-related equiva-
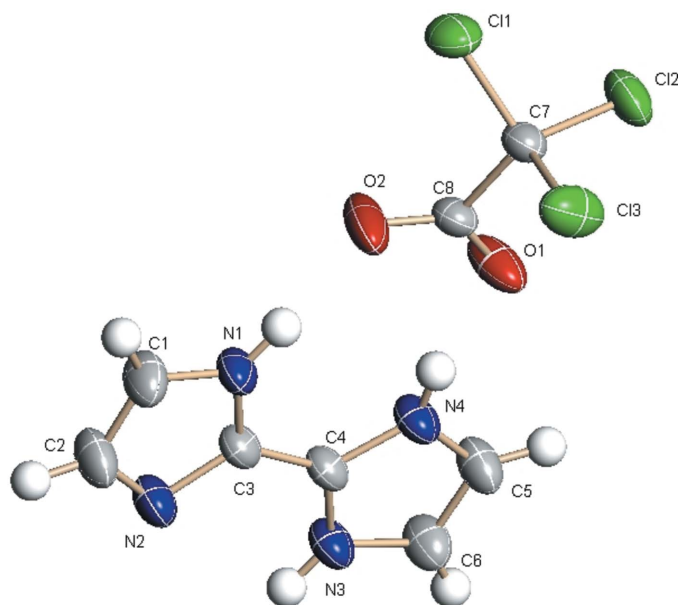
Figure 1
The ion pair of (I), with the atom numbering, showing displacement ellipsoids at the 50% probability level.

lent [Table 2; symmetry code: (i) $2 - x$, $1 - y$, $1 - z$]. The hydrogen-bonding pattern, as shown in Fig. 2, can be described in graph-set motifs (Etter, 1990; Grell *et al.*, 2000) as $R_2^2(9)$ and $R_2^2(10)$. Adjacent dimers are associated by π–π interactions between the five-membered rings of the H₃biim⁺ cations [at (x, y, z) and $(2 - x, -y, 1 - z)$], with the ring centroids separated by 3.861 (1) Å, forming a ribbon-like supramolecular array along the *b* axis (Fig. 3).

Experimental

2,2′-Biimidazole (2 mmol, 0.28 g) was suspended in water (30 ml). To the resulting suspension, concentrated aqueous trichloroacetic acid was added until the suspension became clear. The resulting solution was filtered and allowed to evaporate slowly at room temperature. After three weeks, colourless crystals of (I) appeared.
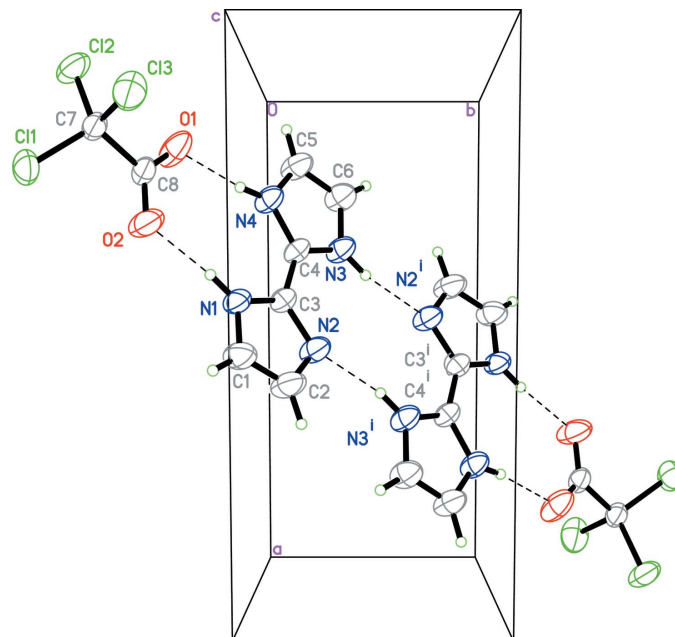
Crystal data

$C_6H_7N_4^+ \cdot C_2Cl_3O_2^-$	$D_x = 1.679$ Mg m^{-3}
$M_r = 297.53$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1438
$a = 12.4010$ (13) Å	reflections
$b = 5.5664$ (6) Å	$\theta = 2.6$–24.2°
$c = 17.3648$ (18) Å	$\mu = 0.77$ mm^{-1}
$\beta = 100.858$ (2)°	$T = 298$ (2) K
$V = 1177.2$ (2) Å^3	Block, colourless
$Z = 4$	$0.31 \times 0.13 \times 0.12$ mm

Data collection

Bruker APEX area-detector diffractometer	2129 independent reflections
	1812 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.031$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$\theta_{max} = 25.3°$
$T_{min} = 0.796$, $T_{max} = 0.913$	$h = -14 \rightarrow 14$
5901 measured reflections	$k = -6 \rightarrow 6$
	$l = -20 \rightarrow 15$

Figure 2
The $R_2^2(9)$ and $R_2^2(10)$ hydrogen-bonding motifs in (I), formed by N—H···O and N—H···N hydrogen-bond interactions, which are shown as dashed lines. [Symmetry code: (i) $2 - x$, $1 - y$, $1 - z$.]
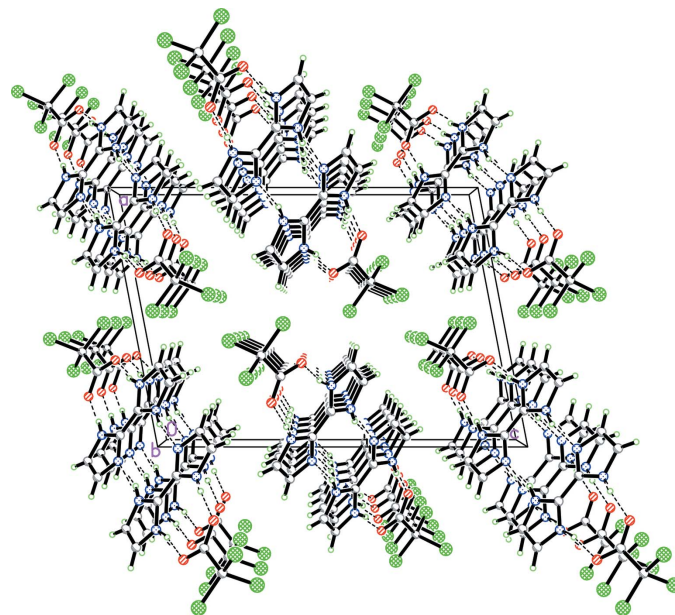
Figure 3
A perspective view, along the *b* axis, of the supramolecular array in (I).

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$+ 0.9103P]$
$wR(F^2) = 0.124$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} < 0.001$
2129 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
163 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C8	1.221 (4)	N3—C6	1.373 (4)
O2—C8	1.222 (4)	N4—C4	1.335 (4)
N1—C3	1.338 (4)	N4—C5	1.363 (4)
N1—C1	1.359 (4)	C1—C2	1.341 (5)
N2—C3	1.325 (4)	C3—C4	1.443 (4)
N2—C2	1.368 (4)	C5—C6	1.330 (5)
N3—C4	1.324 (4)	C7—C8	1.559 (4)
C3—N1—C1	107.4 (3)	N3—C4—N4	108.1 (3)
C3—N2—C2	104.7 (3)	N3—C4—C3	125.1 (3)
C4—N3—C6	108.3 (3)	N4—C4—C3	126.8 (3)
C4—N4—C5	108.6 (3)	C6—C5—N4	107.4 (3)
C2—C1—N1	106.2 (3)	C5—C6—N3	107.6 (3)
C1—C2—N2	110.5 (3)	O1—C8—O2	128.6 (3)
N2—C3—N1	111.3 (3)	O1—C8—C7	115.9 (3)
N2—C3—C4	123.9 (3)	O2—C8—C7	115.4 (3)
N1—C3—C4	124.7 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O2	0.85 (2)	1.85 (2)	2.688 (4)	172 (3)
N3—H3$A\cdots$N2^{i}	0.84 (2)	2.00 (2)	2.811 (4)	163 (3)
N4—H4$A\cdots$O1	0.85 (2)	1.79 (2)	2.630 (4)	167 (3)

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

The H atoms of all N atoms were located in difference density maps and refined, with N—H distances restrained to 0.85 (2) Å and with U_{iso}(H) = $1.2U_{eq}$(N). The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of Csp^2—H = 0.93 Å and with U_{iso}(H) = $1.2U_{eq}$(parent atom).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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