

Bis(1,2,3-benzotriazolium) chloranilate

Xiang-Gao Meng^{a*} and Jin-Liang Qian^b^aChemistry Department, Central China Normal University, Wuhan 430079, People's Republic of China, and ^bThe Second Middle School of Zhi-le Country, Yan-ling County, Xu-Chang 461232, People's Republic of ChinaCorrespondence e-mail:
mengxianggao@mail.cnu.edu.cn

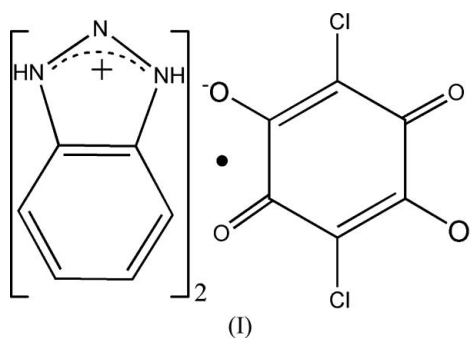
Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.052
 wR factor = 0.139
Data-to-parameter ratio = 13.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $2\text{C}_6\text{H}_6\text{N}_3^+ \cdot \text{C}_6\text{Cl}_2\text{O}_4^{2-}$, the chloranilate dianion lies on an inversion centre. Ions are linked by three $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds into layers in the form of a (4,4)-net built up from $R_8^6(32)$ and $R_1^2(5)$ rings. The layers are further linked into a three-dimensional network by $\pi-\pi$ stacking interactions.

Comment

Supramolecular chemistry remains one of the most active research areas at the forefront of chemistry and biology (Leininger *et al.*, 2000). Much of the fundamental work in current crystal engineering is geared toward developing reliable supramolecular reactions (Aakeröy *et al.*, 2001, 2002). As a continuation of our studies on the molecular and supramolecular structures in cocrystals of organic salts (Liu & Meng, 2006), we now report our findings on the title compound, (I).



The title compound crystallizes with one benzotriazolium cation in a general position and one-half chloranilate dianion, with an inversion centre at the centre of the benzene ring (Fig. 1 and Table 1). As expected, (I) exists as an organic salt, with the H atoms of the chloranilic hydroxyl groups being transferred to the triazole N atoms.

The supramolecular structure of (I), based on $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds and aromatic $\pi-\pi$ interactions, is very similar to that recently reported to be present in the complex between a chloranilic acid dianion and a 4-methylimidazole cation (Wang & Wei, 2005). It is convenient to analyse the formation of the three-dimensional supramolecular network in (I) in terms of layers running parallel to the (100) plane. Atom N1 forms a three-centre hydrogen bond, *via* H1, with the two carbonyl O atoms of the anion at $(1+x, y, z)$, building a $R_1^2(5)$ ring. In addition, triazole atom N3 acts as a donor, *via* H3A, to carbonyl O2 atom in the anion located at $(x+1, -y+\frac{3}{2}, z+\frac{1}{2})$. Expanding hydrogen bonds generate the (100) reference sheet

Received 2 August 2006
Accepted 23 August 2006

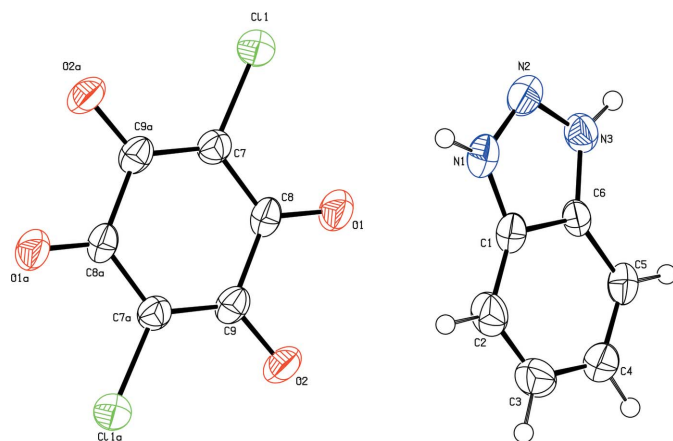


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms labeled with the suffix 'a' are located at the equivalent position $(-x, 1 - y, -z)$.

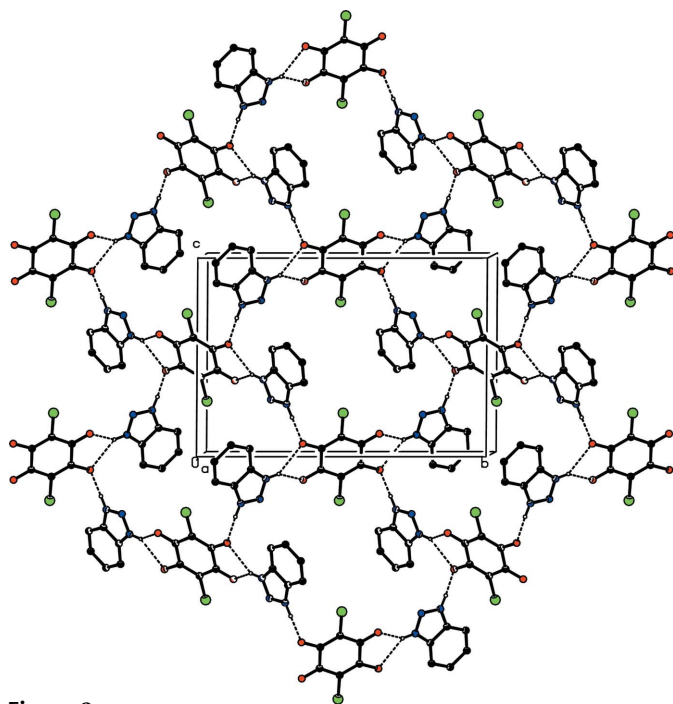


Figure 2

Part of the crystal structure of (I), showing the formation of a layer of $R_8^6(32)$ and $R_1^5(5)$ rings parallel to (100). The supramolecular structure is generated by $N-H \cdots O$ hydrogen bonds (dotted bonds). For the sake of clarity, H atoms bonded to C atoms have been omitted.

in the domain bounded by $-0.235 < x < 2.235$ (Fig. 2), in the form of a (4,4)-net (Batten & Robson, 1998), built up from a combination of $R_8^6(32)$ and $R_1^5(5)$ rings.

The only effective direction-specific interaction between adjacent layers is a π - π stacking interaction between symmetry-related cations at (x, y, z) and $(x - 1, y, z)$ (Fig. 3). The dihedral angle between interacting rings is only $1.4 (1)^\circ$, with an interplanar spacing of $3.272 (1) \text{ \AA}$ and a centroid-to-centroid separation of $3.517 (2) \text{ \AA}$. The π - π stacking interactions link the reference cation at (x, y, z) , which forms part of the hydrogen-bonded layer at $-0.235 < x < 2.235$, with two

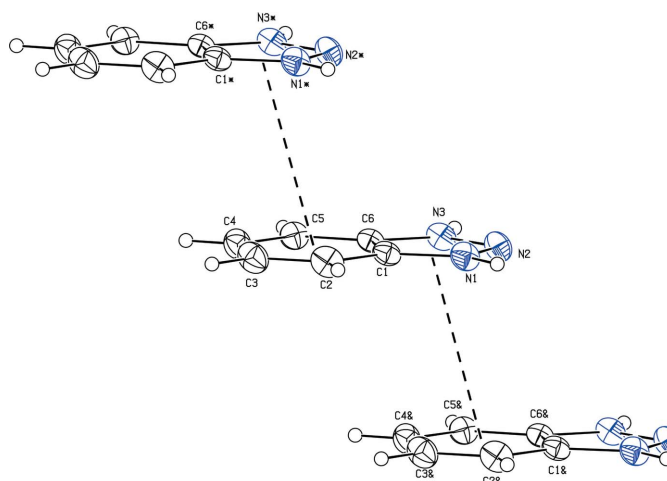


Figure 3

The packing structure of 1,2,3-benzotriazolium cations, showing the π - π interactions (dashed lines) along the [100] direction. Atoms marked with an asterisk (*) and ampersand (&) are at equivalent positions $(x - 1, y, z)$ and $(x + 1, y, z)$, respectively.

cations at $(x - 1, y, z)$ and $(x + 1, y, z)$, which lie in the hydrogen-bonded layers at $-1.235 < x < 1.235$ and $0.765 < x < 3.235$, respectively. The effect of this interaction is to link the layers parallel to (100) into a three-dimensional network.

Experimental

Reagents and solvents were used as obtained without further purification. Chloranilic acid (1 mmol, 0.21 g) and 1,2,3-benzotriazole (1 mmol, 0.12 g) were dissolved in methanol (30 ml). The mixture was stirred for 30 min. at 298 K and then filtered. The resulting clear red solution was kept in air for two weeks. Crystals of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel.

Crystal data

$2C_6H_6N_3^+ \cdot C_6Cl_2O_4^{2-}$
 $M_r = 447.24$
 Monoclinic, $P2_1/c$
 $a = 4.4423 (13) \text{ \AA}$
 $b = 17.401 (5) \text{ \AA}$
 $c = 11.851 (3) \text{ \AA}$
 $\beta = 96.882 (5)^\circ$
 $V = 909.5 (4) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.633 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.40 \text{ mm}^{-1}$
 $T = 292 (2) \text{ K}$
 Plate, red
 $0.30 \times 0.05 \times 0.02 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.890$, $T_{\max} = 0.992$

4958 measured reflections
 1964 independent reflections
 1338 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$
 $\theta_{\max} = 27.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.139$
 $S = 0.99$
 1964 reflections
 142 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0711P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1–N1	1.352 (4)	C8–O1	1.225 (3)
C6–N3	1.363 (3)	C8–C9	1.522 (4)
C7–C9 ⁱ	1.370 (4)	C9–C7 ⁱ	1.370 (4)
C7–C8	1.429 (4)	N1–N2	1.317 (3)
C7–Cl1	1.736 (3)	N2–N3	1.309 (3)
C9 ⁱ –C7–C8	123.2 (2)	N2–N1–C1	112.3 (2)
C7–C8–C9	118.6 (2)	N2–N3–C6	111.5 (2)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 \cdots O1 ⁱⁱ	0.86 (1)	2.00 (1)	2.761 (3)	148 (3)
N1–H1 \cdots O2 ⁱⁱ	0.86 (1)	2.35 (2)	3.041 (3)	138 (3)
N3–H3A \cdots O2 ⁱⁱⁱ	0.86 (1)	1.74 (1)	2.592 (3)	169 (3)

Symmetry codes: (ii) $x + 1, y, z$; (iii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$.

Aromatic H atoms were placed at idealized positions and refined with C–H distances constrained to 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Triazole H atoms H1 and H3A were located in a difference map and

refined with N–H distances restrained to 0.86 (1) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE-Plus* (Bruker, 2001); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

This work was supported mostly by Key Fundamental Project (No. 2002CCA00500).

References

- Aakeröy, C. B., Beatty, A. M. & Helfrich, B. A. (2001). *Angew. Chem. Int. Ed.* **40**, 3240–3242.
- Aakeröy, C. B., Beatty, A. M. & Helfrich, B. A. (2002). *J. Am. Chem. Soc.* **124**, 14425–14432.
- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
- Bruker (2001). *SAINTE-Plus* (Version 6.45), *SMART* (Version 5.628) and *SADABS* (Version 2.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Leininger, S., Olenyuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–908.
- Liu, Z.-X. & Meng, X.-G. (2006). *Acta Cryst. E* **62**, o1286–o1288.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Wang, Z.-L. & Wei, L.-H. (2005). *Acta Cryst. E* **61**, o3129–o3130.