

7-Methoxy-2,3-dioxo-1,4-dihydro-
quinoxalin-6-aminium chloride mono-
hydrateJürgen Brüning,^a Alexander Peters,^a Jan W. Bats^b and
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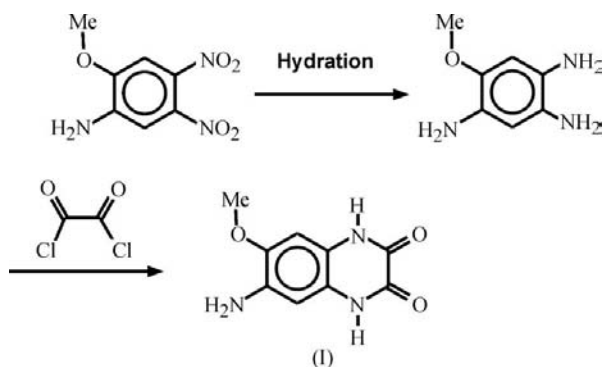
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Single crystals of the title compound, $C_9H_{10}N_3O_3^+ \cdot Cl^- \cdot H_2O$, were obtained by recrystallization from hydrochloric acid. The cations stack along the crystallographic *a* direction. The 2,3-dioxo-1,4-dihydroquinoxaline group shows a significant deviation from planarity [r.m.s. deviation from the best plane = 0.063 (2) Å]. Hydrogen bonding links the cations, chloride anions and water molecules to form an extended three-dimensional architecture.

Comment

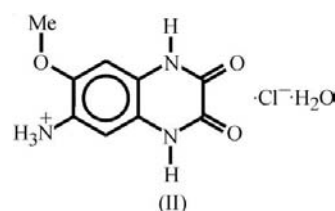
The compound 6-amino-7-methoxy-1,4-dihydroquinoxaline-2,3-dione, (I) (see scheme), is an intermediate in the synthesis of quinoxaline-based azo pigments (Herbst & Hunger, 1995; Alfter *et al.*, 1996; Dietz *et al.*, 2001; Schupp *et al.*, 2002; Blum *et al.*, 2004; Schweikart *et al.*, 2007). Compound (I) is synthesized



from 2,4,5-triamino-1-methoxybenzene and oxalyl chloride. Research on quinoxaline pigments led to Pigment Yellow 213 (Metz & Weber, 1998; Stengel-Rutkowski & Metz, 2000; Metz & Morgenroth, 2009; Schmidt *et al.*, 2009) which is used in water-based automotive coatings. Compound (I) is a dull

yellow powder which is poorly soluble; hence, no single crystals have, to date, been grown.

In order to grow crystals of (I) and determine its crystal structure, as well as to search for different crystallographic phases, hydrates or solvates, a polymorph screening was performed. Therefore, different crystallization methods were used, including (i) recrystallization from various solvents and solvent mixtures by heating and subsequent slow cooling, (ii) overlaying a solution of the compound by an antisolvent, (iii) diffusion of an antisolvent into a solution of the compound *via* the gas phase. The solvents included the most common organic solvents, *e.g.* dimethyl sulfoxide, *N*-methylpyrrolidone, ethers, esters, alcohols, acids and water. According to X-ray powder diffraction, only two phases, *viz.* the industrially produced and the hydrochloride monohydrate phase, (II), have been found.



Single crystals of the title compound, (II), could be obtained by recrystallizing compound (I) in hydrochloric acid (5 *M*). The molecular structure is shown in Fig. 1. The 2,3-dioxo-1,4-dihydroquinoxaline group shows a significant distortion from planarity. The r.m.s. deviation from the best plane, excluding the H atoms, is 0.063 (2) Å. The largest deviation from the best plane is found for atoms O3, C5 and C7 [0.126 (2), 0.088 (2) and 0.089 (2) Å, respectively]. The benzene ring is less distorted [mean deviation from the plane = 0.015 (2) Å] than the pyrazine ring [mean deviation from the plane = 0.022 (2) Å]. The angle between the planes of the two six-membered rings is 4.0 (1)°. To check whether this distortion from planarity is common for this group or if it may result

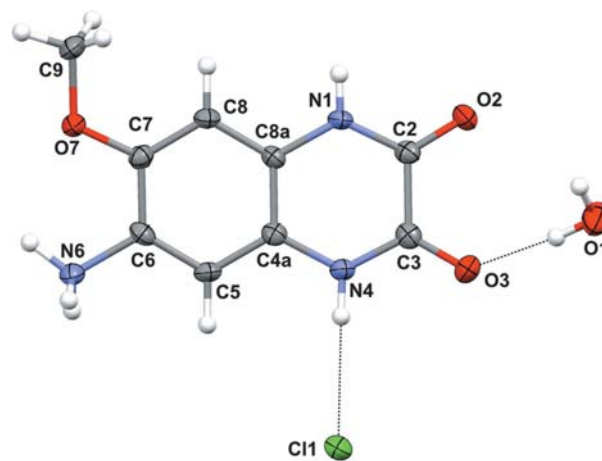


Figure 1

The molecular structure of compound (II), showing atom labels and anisotropic displacement ellipsoids (drawn at the 50% probability level) for non-H atoms.

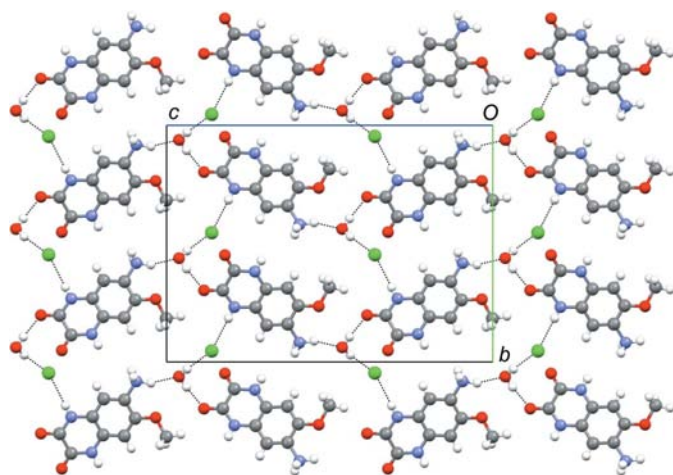


Figure 2

A section of the molecular packing of compound (II), showing the hydrogen-bond architecture; the view direction is [100]. Only the upper layer of molecules is shown. Hydrogen bonds are drawn as dashed lines.

from crystal-packing forces, the planarity of all 28 entries in the Cambridge Structural Database (CSD; Allen, 2002) containing the 2,3-dioxo-1,4-dihydroquinoxaline group was calculated. The results are listed in Table 1. In those cases where a crystal structure has been determined more than once, very similar values are obtained, showing that the values reported in Table 1 may be very reliable. The r.m.s. displacement ranges from 0.005 to 0.071 Å. The nonplanarity of the title compound is in the upper range. Only one compound shows a larger distortion. The large variation among the compounds suggests that the deviation from planarity is considerably affected by crystal-packing forces. This observation is further supported by the fact that rather different deviations from planarity are observed in crystal structures that contain independent molecules (refcodes CNIXQX, RAVFUQ and RAVGAX; Table 1) or in different hydrates of the same compound (refcodes SUHHEI, RAVFOK and RAVFUQ; Table 1). In most structures, the 2,3-dioxo-1,4-dihydroquinoxaline groups form stacks. In some structures, the 2,3-dioxo-1,4-dihydroquinoxaline groups lie in pairs with their molecular planes aligned. Only a few structures do not show a parallel arrangement of the molecular planes. The nonplanarity of the 2,3-dioxo-1,4-dihydroquinoxaline group, however, does not depend on whether the molecules align in stacks or not.

The crystal structure of the title compound is shown in Fig. 2. The molecules stack along the crystallographic *a* direction. Adjacent molecules in the stack are related by *a*-glide planes. The angle between neighbouring 2,3-dioxo-1,4-dihydroquinoxaline planes in the stack is 3.0 (1)°. The smallest interplanar C...C distance in the stack is 3.247 (4) Å between C2 and C8a($x - \frac{1}{2}, y, -z + \frac{1}{2}$). There is also a short intermolecular contact distance of 3.188 (4) Å between O3 and C7($x - \frac{1}{2}, y, -z + \frac{1}{2}$). The methoxy group of (II) is almost coplanar with the bicyclic system; the torsion angle C8–C7–O7–C9 is –9.5 (4)°.

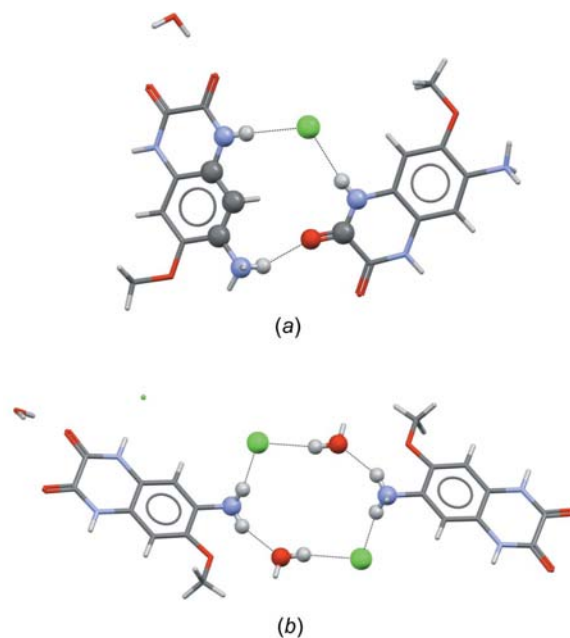


Figure 3

Third-order graph sets (a) $R_3^2(12)$ and (b) $R_6^4(12)$ of compound (II). The atoms involved are highlighted and appendant hydrogen bonds are drawn as dashed lines.

The cations, chloride anions and water molecules are connected by a three-dimensional framework of hydrogen bonds involving O–H...Cl[−], N–H...Cl[−], O–H...O and N–H...O interactions (Table 2). The N6–H6B bond is a donor of a bifurcated hydrogen bond, *viz.* an intermolecular hydrogen bond to a water molecule and an intramolecular hydrogen bond to the methoxy O atom. The water molecule is a donor of two hydrogen bonds and an acceptor of one hydrogen bond. The Cl[−] anion accepts hydrogen bonds from three different cations and from a water molecule.

The most prominent features of the hydrogen-bond network are two 12-membered rings. The first is built from two cations and one chloride anion (Fig. 3a). According to graph-set notation (Etter, 1990; Bernstein *et al.*, 1995) this ring, containing two acceptors and three donors, is denoted as $R_3^2(12)$. The second ring is an $R_6^4(12)$ ring built from two cations, two chloride anions and two water molecules (Fig. 3b). A full graph-set analysis revealed 56 graph sets for first-, second- and third-order level. Selected graph sets for chain and ring sets are shown in Table 3. C–H...O interactions were not included in this analysis as they are much weaker than the interactions of NH and OH groups. For other quinoxalinedione derivatives, extensive graph-set analyses are reported in an earlier work (Kubicki *et al.*, 1996). These graph sets are considerably different to those found for compound (II).

The title compound contains two amide (CONH) groups in a *cis* conformation. Generally, *cis*-amide groups form eight-membered $R_2^2(8)$ rings or $C_2^2(8)$ chains, as observed, for example, in many benzimidazolone derivatives (van de Streek *et al.*, 2009). In contrast, the *cis*-amide groups of compound (II) show neither a ring, nor a chain motif with another amide

group, but both NH groups form hydrogen bonds with the chloride anion. This can be explained by the negative charge of the chloride anion which makes the chloride anion a much better hydrogen-bond acceptor than the carbonyl group of an amide fragment.

Experimental

The raw material of compound (I) was industrially produced, and obtained from Clariant GmbH, Germany. In a flask, (I) (30 mg) was dissolved in a mixture of concentrated hydrochloric acid and water (4 ml, 1:1 v/v). The mixture was subsequently placed in an oven at 343 K to slowly concentrate the solution. After 48 h, yellow-brown rod-shaped crystals of compound (II), with sizes of about $0.6 \times 0.06 \times 0.05$ mm, were obtained.

Crystal data

$C_9H_{10}N_3O_3^+ \cdot Cl^- \cdot H_2O$	$V = 2221.5$ (8) Å ³
$M_r = 261.67$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 6.7339$ (11) Å	$\mu = 0.35$ mm ⁻¹
$b = 15.469$ (4) Å	$T = 168$ K
$c = 21.327$ (4) Å	$0.60 \times 0.06 \times 0.05$ mm

Data collection

Siemens SMART 1K CCD diffractometer	30122 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2000)	2609 independent reflections
$T_{\min} = 0.890$, $T_{\max} = 0.983$	1375 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.153$

Table 1

Mean deviation from the 2,3-dioxo-1,4-dihydroquinoxaline plane.

For structures with more than one molecule in the asymmetric unit, multiple entries are given.

Compound/refcode	Deviation (Å)
Title compound	0.063 (2)
BAKGOJ	0.024
BAKGOJ01	0.023
CAHXQX	0.034
CNIXQX	0.053/0.071
HIHZUT	0.030
HIJBAD	0.048/0.055
HIJBIL	0.028
HIJBOR	0.006
HQOXDO	0.027
HQOXDO01	0.027
HQOXDO02	0.027
OCUSOU	0.021
QERCOF	0.016
RAVFEA	0.016
RAVFIE	0.014/0.015
RAVFOK	0.005
RAVFOK01	0.005
RAVFUQ	0.015/0.021/0.046
RAVGAX	0.019/0.043
RAVGAX01	0.019/0.045
RAVGEB	0.024
SUHHEI	0.012
SUHHIM	0.030
TASWAL	0.046
ZILROB	0.030
ZILRUH	0.053
ZILSAO	0.045
QODCAO	0.025

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N4—H4A \cdots Cl1	0.88	2.36	3.240 (3)	173
N1—H1A \cdots Cl1 ⁱ	0.88	2.37	3.243 (2)	171
N6—H6A \cdots O2 ⁱⁱ	0.91	2.05	2.787 (3)	137
N6—H6B \cdots O7	0.91	2.26	2.708 (3)	110
N6—H6B \cdots O1 ⁱⁱⁱ	0.91	1.96	2.811 (3)	154
N6—H6C \cdots Cl1 ^{iv}	0.91	2.25	3.140 (3)	166
O1—H1B \cdots O3	0.87 (4)	1.91 (4)	2.773 (3)	175 (4)
O1—H1C \cdots Cl1 ^v	0.93 (4)	2.30 (4)	3.209 (3)	169 (3)

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

Table 3

Selected graph sets of compound (II).

First-order	Second-order	Third-order (chain)	Third-order (ring)
C(9)	$C_2^1(7)$	$C_3^2(8)$	$R_3^2(12)^a$
	$C_2^1(8)$	$C_3^2(9)$	$R_3^2(12)^b$
	$C_2^1(9)$	$C_3^2(10)$	$R_6^0(18)$
	$C_2^2(10)$	$C_3^2(11)$	$R_3^2(24)$
		$C_3^2(12)$	$R_3^2(26)$
		$C_3^2(14)$	$R_6^0(38)$
		$C_3^2(17)$	
		$C_3^2(18)$	

Note: (a) and (b) denote Figs. 3(a) and 3(b), respectively.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.117$

$S = 0.99$

2609 reflections

164 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.30$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

The H atoms of the water molecule were taken from a difference synthesis and refined. H atoms on C and N atoms were also taken from a difference synthesis but were then idealized and refined as rigid rotors for N6 and C9 and using a riding model for aromatic C—H, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for planar C, C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl C, N—H = 0.88 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ for planar N, and N—H = 0.91 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ for tetrahedral N atoms.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3132). Services for accessing these data are described at the back of the journal.

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