

1,2-Diazinium hydrogen chloranilate

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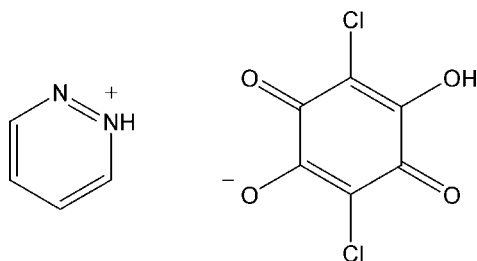
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.082; data-to-parameter ratio = 18.4.

In the crystal structure of the title compound, $\text{C}_4\text{H}_5\text{N}_2^+\cdot\text{C}_6\text{HCl}_2\text{O}_4^-$, there are three crystallographically independent 1,2-diazinium cations and hydrogen chloranilate anions. The anions are held together by pairs of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to form two types of dimers, one of which is centrosymmetric. The 1,2-diazinium cations are linked on both sides of each dimer *via* bifurcated $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to give two kinds of 2–2 cation–anion associations. The 2–2 associations are linked by intermolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds, forming a molecular tape along the [230] direction. The tapes are further connected by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a three-dimensional network.

Related literature

For general background, see: Gotoh *et al.* (2007). For related compounds, see: Gotoh *et al.* (2008); Ishida & Kashino (1999).



Experimental

Crystal data

$\text{C}_4\text{H}_5\text{N}_2^+\cdot\text{C}_6\text{HCl}_2\text{O}_4^-$
 $M_r = 289.07$
 Monoclinic, $P2_1/c$
 $a = 25.6849$ (10) Å
 $b = 7.0516$ (2) Å
 $c = 18.1388$ (6) Å
 $\beta = 97.5822$ (13)°

$V = 3256.56$ (18) Å³
 $Z = 12$
 Mo $K\alpha$ radiation
 $\mu = 0.61$ mm⁻¹
 $T = 173$ (1) K
 $0.40 \times 0.22 \times 0.12$ mm

Data collection

Rigaku R-Axis RAPIDII
 diffractometer
 Absorption correction: numerical
 (ABSCOR; Higashi, 1999)
 $T_{\min} = 0.855$, $T_{\max} = 0.930$

42942 measured reflections
 9398 independent reflections
 7981 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.082$
 $S = 1.04$
 9398 reflections
 511 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1–H1 ⁱ ···O2	0.889 (17)	1.753 (17)	2.6138 (13)	162.2 (17)
N1–H1 ⁱ ···O3	0.889 (17)	2.578 (18)	3.1583 (14)	123.7 (14)
N3–H3 ⁱ ···O6	0.886 (18)	1.811 (17)	2.6621 (13)	160.4 (17)
N3–H3 ⁱ ···O7	0.886 (18)	2.431 (18)	3.0066 (14)	123.0 (14)
O4–H4 ⁱ ···O1	0.79 (2)	2.26 (2)	2.6619 (13)	113 (2)
O4–H4 ⁱ ···O5	0.79 (2)	1.94 (2)	2.6723 (12)	155 (2)
N5–H5 ⁱ ···O10	0.890 (18)	1.881 (18)	2.7450 (14)	163.2 (16)
N5–H5 ⁱ ···O11	0.890 (18)	2.410 (17)	2.9659 (13)	120.7 (14)
O8–H8 ⁱ ···O1	0.80 (2)	1.86 (2)	2.5930 (12)	152 (2)
O8–H8 ⁱ ···O5	0.80 (2)	2.25 (2)	2.6582 (13)	112.7 (18)
O12–H12 ⁱ ···O9	0.79 (2)	2.23 (2)	2.6595 (13)	115.1 (18)
O12–H12 ⁱ ···O9 ⁱⁱ	0.79 (2)	2.02 (2)	2.6801 (12)	142 (2)
C20–H20 ⁱ ···O2 ⁱⁱ	0.95	2.57	3.1097 (15)	116
C21–H21 ⁱ ···O3 ⁱⁱⁱ	0.95	2.36	3.2754 (15)	162
C22–H22 ⁱ ···O3	0.95	2.60	3.1913 (15)	121
C25–H25 ⁱ ···O10	0.95	2.47	3.4056 (15)	169
C26–H26 ⁱ ···O7	0.95	2.44	3.0363 (15)	121
C26–H26 ⁱ ···N6	0.95	2.51	3.2665 (17)	137
C27–H27 ⁱ ···O7	0.95	2.37	3.2765 (15)	159
C28–H28 ⁱ ···O6 ^{iv}	0.95	2.47	3.1091 (15)	124
C30–H30 ⁱ ···O11	0.95	2.34	2.9551 (15)	122

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

Data collection: *PROCESS-AUTO* (Rigaku/MS, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2158).

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supplementary materials

Acta Cryst. (2008). E64, o2095 [doi:10.1107/S1600536808031978]

1,2-Diazinium hydrogen chloranilate

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Comment

The title compound, (I), was prepared in order to extend our study on $D-H\cdots A$ hydrogen bonding ($D = N, O, \text{ or } C; A = N, O \text{ or } Cl$) in amine-chloranilic acid (systematic name: 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) systems (Gotoh *et al.*, 2007). The crystal structure of 1,2-diazine (pyridazine)-chloranilic acid (2/1) was already reported (Ishida & Kashino, 1999; Gotoh *et al.*, 2008).

The asymmetric unit in (I) contains three 1,2-diazinium cations and three hydrogen chloranilate anions. Hydrogen chloranilate anions are held together by $O-H\cdots O$ hydrogen bonds (Table 1) to form two crystallographically independent dimers. The 1,2-diazinium cations are linked on both sides of each dimer *via* bifurcated $N-H\cdots O$ hydrogen bonds to give centro- and acentrosymmetric 2:2 salts of 1,2-diazine and chloranilic acid (Fig. 1). The $N\cdots O$ distances [2.6138 (13)–3.1583 (14) Å] in the hydrogen bonds are longer than those [2.582 (3) Å at 299 K (Ishida & Kashino, 1999) and 2.5549 (12) Å at 110 K (Gotoh *et al.*, 2008)] in 1,2-diazine-chloranilic acid (2/1) and the H atoms are located at the N atom sites. The dihedral angles between C1–C6 and C7–C12 rings, C1–C6 and N1/N2/C19–C22 rings, C7–C12 and N3/N4/C23–C26 rings, and C13–C18 and N5/N6/C27–C30 rings are 3.40 (5), 11.83 (5), 4.88 (6) and 11.41 (5)°, respectively. The 2:2 units are linked by intermolecular $C-H\cdots O$ and $C-H\cdots N$ hydrogen bonds, forming a molecular tape along the [230] direction. The tapes are further connected by $C-H\cdots O$ hydrogen bonds, forming a three-dimensional network (Table 1 and Fig. 2).

Experimental

Single crystals were obtained by slow evaporation from a methanol solution (30 ml) of chloranilic acid (400 mg) and 1,2-diazine (155 mg).

Refinement

C-bound H atoms were positioned geometrically ($C-H = 0.95$ Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms in the $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds were located in a difference Fourier map and refined isotropically (refined distances given in Table 1).

Figures

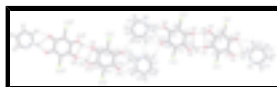


Fig. 1. The structure of the 2:2 units of (I). The dashed lines indicate $O-H\cdots O$, $C-H\cdots O$ and $C-H\cdots N$ hydrogen bonds (symmetry code as Table 1). Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.

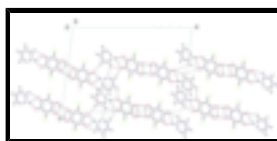
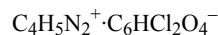


Fig. 2. A partial packing diagram of (I), viewed down the b axis. The dashed lines indicate $O-H\cdots O$, $C-H\cdots O$ and $C-H\cdots N$ hydrogen bonds.

1,2-Diazinium hydrogen chloranilate

Crystal data

 $M_r = 289.07$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 25.6849 (10) \text{ \AA}$ $b = 7.0516 (2) \text{ \AA}$ $c = 18.1388 (6) \text{ \AA}$ $\beta = 97.5822 (13)^\circ$ $V = 3256.56 (18) \text{ \AA}^3$ $Z = 12$ $F_{000} = 1752.00$ $D_x = 1.769 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.71075 \text{ \AA}$

Cell parameters from 36292 reflections

 $\theta = 3.0\text{--}30.0^\circ$ $\mu = 0.61 \text{ mm}^{-1}$ $T = 173 (1) \text{ K}$

Prism, brown

 $0.40 \times 0.22 \times 0.12 \text{ mm}$

Data collection

Rigaku R-Axis RAPIDII
diffractometerDetector resolution: $10.00 \text{ pixels mm}^{-1}$ ω scansAbsorption correction: numerical
(ABSCOR; Higashi, 1999) $T_{\min} = 0.855$, $T_{\max} = 0.930$

42942 measured reflections

9398 independent reflections

7981 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.025$ $\theta_{\text{max}} = 30.0^\circ$ $h = -36 \rightarrow 36$ $k = -9 \rightarrow 8$ $l = -24 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.030$ $wR(F^2) = 0.082$ $S = 1.04$

9398 reflections

511 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sitesH atoms treated by a mixture of
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.8542P]$$

where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.002$ $\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.788813 (11)	1.00777 (4)	0.695195 (15)	0.02287 (7)
C12	0.813873 (11)	1.33053 (4)	0.375637 (15)	0.01939 (6)
C13	0.546309 (11)	0.98926 (4)	0.291828 (15)	0.02164 (7)
C14	0.529070 (10)	0.68298 (4)	0.616552 (15)	0.01938 (6)
C15	0.134170 (11)	0.31600 (4)	0.406398 (15)	0.02014 (6)
C16	0.126530 (11)	0.00278 (4)	0.732528 (15)	0.02182 (7)
O1	0.70886 (3)	1.03911 (14)	0.56092 (5)	0.02672 (19)
O2	0.88525 (3)	1.17619 (12)	0.64597 (5)	0.02155 (17)
O3	0.89647 (3)	1.29114 (12)	0.50763 (5)	0.02036 (16)
O4	0.71996 (3)	1.15850 (13)	0.42465 (5)	0.02316 (18)
O5	0.62655 (3)	0.99280 (14)	0.42628 (5)	0.0258 (2)
O6	0.45198 (3)	0.80783 (12)	0.34672 (5)	0.02140 (17)
O7	0.44599 (3)	0.69004 (12)	0.48544 (5)	0.02138 (17)
O8	0.61970 (3)	0.86803 (14)	0.56295 (5)	0.02294 (18)
O9	0.04325 (3)	0.14786 (13)	0.47288 (5)	0.02485 (19)
O10	0.22343 (3)	0.29297 (12)	0.53149 (5)	0.02021 (17)
O11	0.21688 (3)	0.17839 (12)	0.67058 (5)	0.02290 (18)
O12	0.04124 (3)	0.00464 (13)	0.60811 (5)	0.02206 (18)
N1	0.97488 (4)	1.35579 (15)	0.65484 (6)	0.0219 (2)
N2	0.99547 (4)	1.31774 (15)	0.72462 (6)	0.0247 (2)
N3	0.36001 (4)	0.64298 (15)	0.35724 (6)	0.0212 (2)
N4	0.33565 (4)	0.66986 (16)	0.28834 (6)	0.0265 (2)
N5	0.31069 (4)	0.37842 (15)	0.63023 (6)	0.02006 (19)
N6	0.34283 (4)	0.45730 (16)	0.58711 (6)	0.0239 (2)
C1	0.75362 (4)	1.09400 (16)	0.55266 (6)	0.0170 (2)
C2	0.79706 (4)	1.09715 (16)	0.60871 (6)	0.01556 (19)
C3	0.84590 (4)	1.16825 (15)	0.59736 (6)	0.0152 (2)
C4	0.85282 (4)	1.24116 (15)	0.51915 (6)	0.01446 (19)
C5	0.80717 (4)	1.24251 (15)	0.46242 (6)	0.01550 (19)
C6	0.76101 (4)	1.16835 (15)	0.47678 (6)	0.0164 (2)
C7	0.58355 (4)	0.92184 (16)	0.43505 (6)	0.0165 (2)
C8	0.54005 (4)	0.90299 (16)	0.37928 (6)	0.0157 (2)
C9	0.49245 (4)	0.82418 (15)	0.39314 (6)	0.0155 (2)

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C10	0.48814 (4)	0.75267 (15)	0.47232 (6)	0.01508 (19)
C11	0.53375 (4)	0.76601 (15)	0.52856 (6)	0.01517 (19)
C12	0.57836 (4)	0.84830 (16)	0.51193 (6)	0.0162 (2)
C13	0.08582 (4)	0.15642 (15)	0.51475 (6)	0.0164 (2)
C14	0.13318 (4)	0.23100 (15)	0.49570 (6)	0.01558 (19)
C15	0.17974 (4)	0.23689 (15)	0.54582 (6)	0.01537 (19)
C16	0.17708 (4)	0.16726 (15)	0.62576 (6)	0.0154 (2)
C17	0.12835 (4)	0.08899 (16)	0.64439 (6)	0.0159 (2)
C18	0.08570 (4)	0.07922 (15)	0.59219 (6)	0.0156 (2)
C19	1.04186 (5)	1.39362 (18)	0.74659 (7)	0.0234 (2)
H19	1.0576	1.3710	0.7962	0.028*
C20	1.06920 (5)	1.50533 (17)	0.70098 (7)	0.0232 (2)
H20	1.1027	1.5564	0.7190	0.028*
C21	1.04646 (5)	1.53937 (18)	0.62952 (7)	0.0231 (2)
H21	1.0637	1.6133	0.5962	0.028*
C22	0.99713 (5)	1.46098 (17)	0.60787 (7)	0.0228 (2)
H22	0.9795	1.4834	0.5592	0.027*
C23	0.28768 (5)	0.59892 (19)	0.27484 (7)	0.0279 (3)
H23	0.2688	0.6165	0.2266	0.034*
C24	0.26300 (5)	0.49954 (18)	0.32732 (8)	0.0250 (3)
H24	0.2286	0.4497	0.3148	0.030*
C25	0.28964 (5)	0.47601 (18)	0.39706 (7)	0.0252 (2)
H25	0.2746	0.4101	0.4347	0.030*
C26	0.33997 (5)	0.55323 (18)	0.41044 (7)	0.0247 (2)
H26	0.3599	0.5409	0.4582	0.030*
C27	0.38814 (5)	0.51986 (19)	0.62180 (7)	0.0252 (3)
H27	0.4118	0.5787	0.5928	0.030*
C28	0.40324 (5)	0.50458 (18)	0.69840 (7)	0.0242 (2)
H28	0.4363	0.5508	0.7209	0.029*
C29	0.36891 (5)	0.42094 (18)	0.74013 (7)	0.0242 (2)
H29	0.3774	0.4059	0.7924	0.029*
C30	0.32121 (5)	0.35891 (18)	0.70316 (7)	0.0238 (2)
H30	0.2961	0.3023	0.7303	0.029*
H1	0.9443 (7)	1.298 (2)	0.6418 (10)	0.040 (5)*
H4	0.6953 (9)	1.112 (3)	0.4388 (13)	0.070 (7)*
H8	0.6436 (8)	0.921 (3)	0.5477 (12)	0.064 (7)*
H3	0.3919 (7)	0.693 (2)	0.3649 (10)	0.037 (5)*
H5	0.2801 (7)	0.340 (2)	0.6060 (10)	0.040 (5)*
H12	0.0205 (8)	-0.001 (3)	0.5722 (11)	0.052 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.02091 (13)	0.03338 (16)	0.01460 (12)	-0.00592 (10)	0.00337 (9)	0.00278 (11)
C12	0.02201 (13)	0.02140 (13)	0.01473 (12)	-0.00058 (9)	0.00235 (9)	0.00273 (10)
C13	0.02047 (13)	0.03130 (15)	0.01329 (12)	-0.00316 (10)	0.00276 (9)	0.00268 (10)
C14	0.02048 (13)	0.02307 (13)	0.01446 (12)	-0.00125 (9)	0.00187 (9)	0.00367 (10)
C15	0.02339 (13)	0.02148 (13)	0.01490 (12)	-0.00022 (10)	0.00008 (9)	0.00332 (10)

C16	0.01993 (13)	0.03180 (15)	0.01370 (12)	-0.00260 (10)	0.00209 (9)	0.00197 (10)
O1	0.0137 (4)	0.0443 (5)	0.0221 (4)	-0.0085 (3)	0.0020 (3)	0.0002 (4)
O2	0.0153 (4)	0.0311 (4)	0.0170 (4)	-0.0058 (3)	-0.0026 (3)	0.0029 (3)
O3	0.0155 (4)	0.0264 (4)	0.0195 (4)	-0.0057 (3)	0.0034 (3)	-0.0006 (3)
O4	0.0137 (4)	0.0360 (5)	0.0185 (4)	-0.0030 (3)	-0.0026 (3)	0.0037 (4)
O5	0.0148 (4)	0.0416 (5)	0.0206 (4)	-0.0087 (3)	0.0009 (3)	0.0036 (4)
O6	0.0156 (4)	0.0296 (4)	0.0177 (4)	-0.0056 (3)	-0.0028 (3)	0.0023 (3)
O7	0.0163 (4)	0.0282 (4)	0.0195 (4)	-0.0075 (3)	0.0020 (3)	0.0000 (3)
O8	0.0135 (4)	0.0372 (5)	0.0169 (4)	-0.0064 (3)	-0.0024 (3)	0.0047 (4)
O9	0.0161 (4)	0.0313 (5)	0.0248 (4)	-0.0035 (3)	-0.0062 (3)	0.0067 (4)
O10	0.0159 (4)	0.0265 (4)	0.0179 (4)	-0.0047 (3)	0.0014 (3)	0.0001 (3)
O11	0.0167 (4)	0.0305 (4)	0.0198 (4)	-0.0041 (3)	-0.0036 (3)	0.0035 (3)
O12	0.0138 (4)	0.0323 (5)	0.0196 (4)	-0.0045 (3)	0.0003 (3)	0.0014 (3)
N1	0.0144 (4)	0.0246 (5)	0.0262 (5)	-0.0023 (4)	0.0010 (4)	-0.0009 (4)
N2	0.0249 (5)	0.0260 (5)	0.0233 (5)	-0.0044 (4)	0.0041 (4)	0.0014 (4)
N3	0.0153 (4)	0.0247 (5)	0.0225 (5)	-0.0032 (4)	-0.0015 (4)	-0.0013 (4)
N4	0.0262 (5)	0.0306 (6)	0.0216 (5)	-0.0059 (4)	-0.0017 (4)	0.0021 (4)
N5	0.0151 (4)	0.0238 (5)	0.0207 (5)	-0.0023 (4)	0.0001 (3)	-0.0016 (4)
N6	0.0214 (5)	0.0310 (5)	0.0189 (5)	-0.0043 (4)	0.0017 (4)	-0.0003 (4)
C1	0.0141 (5)	0.0205 (5)	0.0164 (5)	-0.0015 (4)	0.0018 (4)	-0.0019 (4)
C2	0.0143 (5)	0.0204 (5)	0.0120 (4)	-0.0022 (4)	0.0019 (3)	0.0002 (4)
C3	0.0134 (4)	0.0169 (5)	0.0152 (5)	-0.0013 (4)	0.0012 (4)	-0.0013 (4)
C4	0.0145 (4)	0.0143 (5)	0.0144 (5)	-0.0014 (4)	0.0016 (4)	-0.0022 (4)
C5	0.0159 (5)	0.0170 (5)	0.0133 (4)	0.0005 (4)	0.0009 (4)	0.0004 (4)
C6	0.0142 (5)	0.0188 (5)	0.0155 (5)	0.0014 (4)	-0.0004 (4)	-0.0012 (4)
C7	0.0138 (5)	0.0206 (5)	0.0152 (5)	-0.0011 (4)	0.0014 (4)	0.0002 (4)
C8	0.0152 (5)	0.0195 (5)	0.0123 (4)	-0.0006 (4)	0.0012 (4)	0.0002 (4)
C9	0.0146 (5)	0.0170 (5)	0.0145 (5)	-0.0009 (4)	0.0008 (4)	0.0000 (4)
C10	0.0144 (4)	0.0154 (5)	0.0153 (5)	-0.0014 (4)	0.0013 (4)	-0.0013 (4)
C11	0.0157 (5)	0.0170 (5)	0.0127 (4)	-0.0005 (4)	0.0013 (4)	0.0014 (4)
C12	0.0134 (5)	0.0193 (5)	0.0153 (5)	0.0004 (4)	-0.0006 (4)	-0.0002 (4)
C13	0.0157 (5)	0.0155 (5)	0.0172 (5)	0.0015 (4)	-0.0007 (4)	0.0010 (4)
C14	0.0162 (5)	0.0167 (5)	0.0133 (4)	0.0001 (4)	-0.0001 (4)	0.0014 (4)
C15	0.0156 (5)	0.0143 (5)	0.0158 (5)	-0.0006 (4)	0.0005 (4)	-0.0017 (4)
C16	0.0142 (5)	0.0158 (5)	0.0156 (5)	0.0001 (4)	0.0001 (4)	-0.0010 (4)
C17	0.0151 (5)	0.0186 (5)	0.0140 (5)	0.0001 (4)	0.0016 (4)	-0.0004 (4)
C18	0.0130 (4)	0.0170 (5)	0.0169 (5)	0.0006 (4)	0.0022 (4)	-0.0014 (4)
C19	0.0229 (6)	0.0258 (6)	0.0204 (5)	-0.0011 (4)	-0.0012 (4)	-0.0004 (5)
C20	0.0164 (5)	0.0262 (6)	0.0265 (6)	-0.0046 (4)	0.0017 (4)	-0.0065 (5)
C21	0.0228 (6)	0.0233 (6)	0.0241 (6)	-0.0060 (4)	0.0065 (4)	-0.0004 (5)
C22	0.0205 (5)	0.0246 (6)	0.0224 (6)	0.0013 (4)	-0.0006 (4)	0.0009 (5)
C23	0.0265 (6)	0.0303 (6)	0.0241 (6)	-0.0045 (5)	-0.0075 (5)	0.0015 (5)
C24	0.0164 (5)	0.0265 (6)	0.0309 (6)	-0.0037 (4)	-0.0019 (4)	-0.0038 (5)
C25	0.0213 (6)	0.0293 (6)	0.0252 (6)	-0.0060 (5)	0.0034 (4)	0.0002 (5)
C26	0.0209 (6)	0.0312 (6)	0.0205 (5)	-0.0034 (5)	-0.0034 (4)	0.0011 (5)
C27	0.0204 (6)	0.0325 (6)	0.0231 (6)	-0.0072 (5)	0.0038 (4)	-0.0011 (5)
C28	0.0176 (5)	0.0300 (6)	0.0238 (6)	-0.0038 (4)	-0.0016 (4)	-0.0052 (5)
C29	0.0240 (6)	0.0303 (6)	0.0172 (5)	-0.0025 (5)	-0.0015 (4)	-0.0008 (5)
C30	0.0212 (5)	0.0284 (6)	0.0217 (6)	-0.0041 (4)	0.0030 (4)	0.0003 (5)

supplementary materials

Geometric parameters (Å, °)

C11—C2	1.7293 (11)	C3—C4	1.5412 (15)
C12—C5	1.7218 (11)	C4—C5	1.4545 (14)
C13—C8	1.7262 (11)	C5—C6	1.3522 (15)
C14—C11	1.7192 (11)	C7—C8	1.4110 (14)
C15—C14	1.7305 (11)	C7—C12	1.5102 (15)
C16—C17	1.7168 (11)	C8—C9	1.3958 (15)
O1—C1	1.2408 (13)	C9—C10	1.5398 (15)
O2—C3	1.2517 (13)	C10—C11	1.4515 (14)
O3—C4	1.2193 (13)	C11—C12	1.3533 (15)
O4—C6	1.3218 (13)	C13—C14	1.4096 (15)
O4—H4	0.78 (2)	C13—C18	1.5069 (15)
O5—C7	1.2417 (13)	C14—C15	1.4040 (14)
O6—C9	1.2536 (13)	C15—C16	1.5408 (15)
O7—C10	1.2213 (13)	C16—C17	1.4481 (15)
O8—C12	1.3207 (12)	C17—C18	1.3520 (14)
O8—H8	0.80 (2)	C19—C20	1.3969 (17)
O9—C13	1.2476 (13)	C19—H19	0.9500
O10—C15	1.2491 (13)	C20—C21	1.3708 (17)
O11—C16	1.2218 (13)	C20—H20	0.9500
O12—C18	1.3232 (13)	C21—C22	1.3906 (16)
O12—H12	0.79 (2)	C21—H21	0.9500
N1—C22	1.3158 (16)	C22—H22	0.9500
N1—N2	1.3331 (15)	C23—C24	1.3994 (19)
N1—H1	0.888 (18)	C23—H23	0.9500
N2—C19	1.3189 (15)	C24—C25	1.3666 (18)
N3—C26	1.3144 (16)	C24—H24	0.9500
N3—N4	1.3355 (14)	C25—C26	1.3942 (16)
N3—H3	0.886 (17)	C25—H25	0.9500
N4—C23	1.3223 (16)	C26—H26	0.9500
N5—C30	1.3221 (16)	C27—C28	1.3966 (18)
N5—N6	1.3314 (14)	C27—H27	0.9500
N5—H5	0.891 (18)	C28—C29	1.3690 (17)
N6—C27	1.3236 (15)	C28—H28	0.9500
C1—C2	1.4069 (14)	C29—C30	1.3875 (16)
C1—C6	1.5079 (15)	C29—H29	0.9500
C2—C3	1.3913 (14)	C30—H30	0.9500
C6—O4—H4	113.0 (17)	C14—C13—C18	118.12 (9)
C12—O8—H8	112.9 (16)	C15—C14—C13	122.76 (10)
C18—O12—H12	110.5 (15)	C15—C14—C15	118.65 (8)
C22—N1—N2	125.20 (10)	C13—C14—C15	118.58 (8)
C22—N1—H1	122.0 (12)	O10—C15—C14	125.90 (10)
N2—N1—H1	112.8 (12)	O10—C15—C16	116.70 (9)
C19—N2—N1	115.76 (10)	C14—C15—C16	117.40 (9)
C26—N3—N4	125.10 (10)	O11—C16—C17	122.83 (10)
C26—N3—H3	121.5 (11)	O11—C16—C15	117.95 (10)
N4—N3—H3	113.4 (11)	C17—C16—C15	119.21 (9)

C23—N4—N3	115.44 (11)	C18—C17—C16	120.10 (10)
C30—N5—N6	124.80 (10)	C18—C17—Cl6	120.99 (8)
C30—N5—H5	120.8 (12)	C16—C17—Cl6	118.88 (8)
N6—N5—H5	114.4 (12)	O12—C18—C17	120.69 (10)
C27—N6—N5	115.74 (10)	O12—C18—C13	117.06 (9)
O1—C1—C2	125.21 (10)	C17—C18—C13	122.23 (10)
O1—C1—C6	116.67 (10)	N2—C19—C20	123.68 (11)
C2—C1—C6	118.09 (9)	N2—C19—H19	118.2
C3—C2—C1	122.90 (10)	C20—C19—H19	118.2
C3—C2—C11	119.09 (8)	C21—C20—C19	118.28 (11)
C1—C2—C11	118.00 (8)	C21—C20—H20	120.9
O2—C3—C2	124.89 (10)	C19—C20—H20	120.9
O2—C3—C4	116.93 (9)	C20—C21—C22	117.14 (11)
C2—C3—C4	118.17 (9)	C20—C21—H21	121.4
O3—C4—C5	123.41 (10)	C22—C21—H21	121.4
O3—C4—C3	118.33 (9)	N1—C22—C21	119.91 (11)
C5—C4—C3	118.24 (9)	N1—C22—H22	120.0
C6—C5—C4	120.45 (10)	C21—C22—H22	120.0
C6—C5—Cl2	120.77 (8)	N4—C23—C24	123.93 (12)
C4—C5—Cl2	118.72 (8)	N4—C23—H23	118.0
O4—C6—C5	121.29 (10)	C24—C23—H23	118.0
O4—C6—C1	116.75 (10)	C25—C24—C23	118.30 (11)
C5—C6—C1	121.96 (10)	C25—C24—H24	120.8
O5—C7—C8	125.43 (10)	C23—C24—H24	120.8
O5—C7—C12	116.43 (9)	C24—C25—C26	116.95 (12)
C8—C7—C12	118.14 (9)	C24—C25—H25	121.5
C9—C8—C7	122.55 (10)	C26—C25—H25	121.5
C9—C8—Cl3	119.72 (8)	N3—C26—C25	120.28 (11)
C7—C8—Cl3	117.69 (8)	N3—C26—H26	119.9
O6—C9—C8	125.73 (10)	C25—C26—H26	119.9
O6—C9—C10	116.17 (9)	N6—C27—C28	123.96 (12)
C8—C9—C10	118.09 (9)	N6—C27—H27	118.0
O7—C10—C11	122.72 (10)	C28—C27—H27	118.0
O7—C10—C9	118.35 (9)	C29—C28—C27	117.95 (11)
C11—C10—C9	118.92 (9)	C29—C28—H28	121.0
C12—C11—C10	119.98 (10)	C27—C28—H28	121.0
C12—C11—Cl4	121.19 (8)	C28—C29—C30	117.43 (11)
C10—C11—Cl4	118.79 (8)	C28—C29—H29	121.3
O8—C12—C11	121.01 (10)	C30—C29—H29	121.3
O8—C12—C7	116.74 (9)	N5—C30—C29	120.10 (11)
C11—C12—C7	122.25 (9)	N5—C30—H30	119.9
O9—C13—C14	125.75 (10)	C29—C30—H30	119.9
O9—C13—C18	116.14 (10)		
C22—N1—N2—C19	-0.02 (18)	C10—C11—C12—C7	-2.38 (17)
C26—N3—N4—C23	0.15 (19)	Cl4—C11—C12—C7	179.80 (8)
C30—N5—N6—C27	-0.32 (18)	O5—C7—C12—O8	0.75 (15)
O1—C1—C2—C3	-176.99 (12)	C8—C7—C12—O8	-179.96 (10)
C6—C1—C2—C3	1.03 (16)	O5—C7—C12—C11	-179.30 (11)
O1—C1—C2—Cl1	3.15 (17)	C8—C7—C12—C11	-0.01 (16)

supplementary materials

C6—C1—C2—C11	-178.82 (8)	O9—C13—C14—C15	179.75 (11)
C1—C2—C3—O2	178.89 (11)	C18—C13—C14—C15	-0.34 (16)
C11—C2—C3—O2	-1.25 (16)	O9—C13—C14—C15	-1.12 (16)
C1—C2—C3—C4	-1.82 (16)	C18—C13—C14—C15	178.79 (8)
C11—C2—C3—C4	178.04 (8)	C13—C14—C15—O10	176.55 (11)
O2—C3—C4—O3	4.40 (15)	C15—C14—C15—O10	-2.58 (16)
C2—C3—C4—O3	-174.94 (10)	C13—C14—C15—C16	-3.15 (16)
O2—C3—C4—C5	-177.03 (10)	C15—C14—C15—C16	177.72 (7)
C2—C3—C4—C5	3.63 (14)	O10—C15—C16—O11	2.96 (15)
O3—C4—C5—C6	173.62 (11)	C14—C15—C16—O11	-177.31 (10)
C3—C4—C5—C6	-4.87 (15)	O10—C15—C16—C17	-175.99 (10)
O3—C4—C5—C12	-3.52 (15)	C14—C15—C16—C17	3.74 (15)
C3—C4—C5—C12	177.99 (8)	O11—C16—C17—C18	-179.53 (11)
C4—C5—C6—O4	-176.09 (10)	C15—C16—C17—C18	-0.63 (15)
C12—C5—C6—O4	1.00 (15)	O11—C16—C17—C16	-1.56 (15)
C4—C5—C6—C1	4.23 (16)	C15—C16—C17—C16	177.34 (8)
C12—C5—C6—C1	-178.68 (8)	C16—C17—C18—O12	178.68 (10)
O1—C1—C6—O4	-3.73 (15)	C16—C17—C18—O12	0.75 (15)
C2—C1—C6—O4	178.08 (10)	C16—C17—C18—C13	-3.07 (16)
O1—C1—C6—C5	175.96 (11)	C16—C17—C18—C13	179.00 (8)
C2—C1—C6—C5	-2.23 (16)	O9—C13—C18—O12	1.95 (15)
O5—C7—C8—C9	-179.02 (11)	C14—C13—C18—O12	-177.98 (10)
C12—C7—C8—C9	1.75 (16)	O9—C13—C18—C17	-176.36 (11)
O5—C7—C8—C13	-1.27 (16)	C14—C13—C18—C17	3.71 (16)
C12—C7—C8—C13	179.50 (8)	N1—N2—C19—C20	-0.85 (18)
C7—C8—C9—O6	178.05 (11)	N2—C19—C20—C21	0.50 (19)
C13—C8—C9—O6	0.34 (16)	C19—C20—C21—C22	0.68 (18)
C7—C8—C9—C10	-1.04 (16)	N2—N1—C22—C21	1.20 (19)
C13—C8—C9—C10	-178.74 (8)	C20—C21—C22—N1	-1.48 (18)
O6—C9—C10—O7	-1.84 (15)	N3—N4—C23—C24	-0.8 (2)
C8—C9—C10—O7	177.33 (10)	N4—C23—C24—C25	0.9 (2)
O6—C9—C10—C11	179.47 (10)	C23—C24—C25—C26	-0.24 (19)
C8—C9—C10—C11	-1.36 (15)	N4—N3—C26—C25	0.4 (2)
O7—C10—C11—C12	-175.60 (11)	C24—C25—C26—N3	-0.35 (19)
C9—C10—C11—C12	3.03 (15)	N5—N6—C27—C28	0.92 (19)
O7—C10—C11—C14	2.27 (15)	N6—C27—C28—C29	-0.4 (2)
C9—C10—C11—C14	-179.10 (8)	C27—C28—C29—C30	-0.63 (19)
C10—C11—C12—O8	177.57 (10)	N6—N5—C30—C29	-0.7 (2)
C14—C11—C12—O8	-0.24 (16)	C28—C29—C30—N5	1.20 (19)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O2	0.889 (17)	1.753 (17)	2.6138 (13)	162.2 (17)
N1—H1 \cdots O3	0.889 (17)	2.578 (18)	3.1583 (14)	123.7 (14)
N3—H3 \cdots O6	0.886 (18)	1.811 (17)	2.6621 (13)	160.4 (17)
N3—H3 \cdots O7	0.886 (18)	2.431 (18)	3.0066 (14)	123.0 (14)
O4—H4 \cdots O1	0.79 (2)	2.26 (2)	2.6619 (13)	113 (2)
O4—H4 \cdots O5	0.79 (2)	1.94 (2)	2.6723 (12)	155 (2)

N5—H5…O10	0.890 (18)	1.881 (18)	2.7450 (14)	163.2 (16)
N5—H5…O11	0.890 (18)	2.410 (17)	2.9659 (13)	120.7 (14)
O8—H8…O1	0.80 (2)	1.86 (2)	2.5930 (12)	152 (2)
O8—H8…O5	0.80 (2)	2.25 (2)	2.6582 (13)	112.7 (18)
O12—H12…O9	0.79 (2)	2.23 (2)	2.6595 (13)	115.1 (18)
O12—H12…O9 ⁱ	0.79 (2)	2.02 (2)	2.6801 (12)	142 (2)
C20—H20…O2 ⁱⁱ	0.95	2.57	3.1097 (15)	116
C21—H21…O3 ⁱⁱⁱ	0.95	2.36	3.2754 (15)	162
C22—H22…O3	0.95	2.60	3.1913 (15)	121
C25—H25…O10	0.95	2.47	3.4056 (15)	169
C26—H26…O7	0.95	2.44	3.0363 (15)	121
C26—H26…N6	0.95	2.51	3.2665 (17)	137
C27—H27…O7	0.95	2.37	3.2765 (15)	159
C28—H28…O6 ^{iv}	0.95	2.47	3.1091 (15)	124
C30—H30…O11	0.95	2.34	2.9551 (15)	122

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x+2, y+1/2, -z+3/2$; (iii) $-x+2, -y+3, -z+1$; (iv) $x, -y+3/2, z+1/2$.

Fig. 1

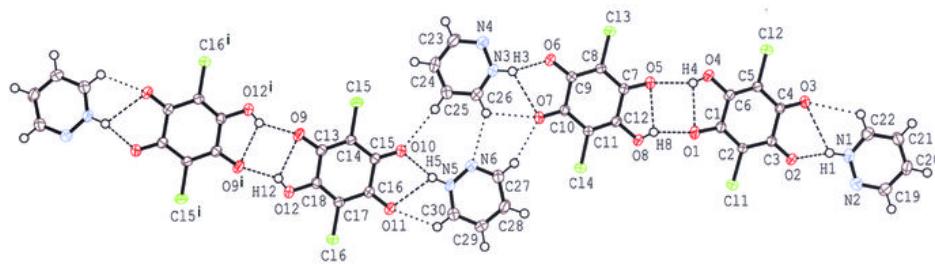


Fig. 2

