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Chloranilic acid: a redetermination at 100 K

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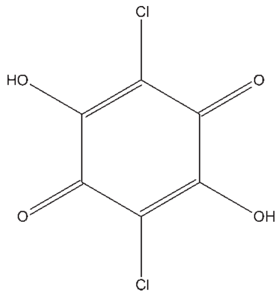
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.025; wR factor = 0.056; data-to-parameter ratio = 13.1.

The crystal structure of chloranilic acid, $C_6H_2Cl_2O_4$, was first described by Andersen in 1967 [Andersen, E. K. (1967). Acta Cryst. **22**, 188–191] at room temperature using visually estimated intensities. Taking into account the importance of the title compound, we have redetermined the structure at 100 (1) K. The approximately planar molecule [the maximum deviation from the mean plane through the ring is 0.0014 (9) Å for the ring atoms and 0.029 (3) Å for the other atoms] occupies a special position, lying across the center of symmetry. In the crystal structure, a two-dimensional hydrogen-bonded network sustained by O—H⋯O interactions runs approximately parallel to [101]. The two-dimensional layers are further packed in a parallel fashion, stabilized by Cl⋯Cl interactions [Cl⋯Cl = 3.2838 (8) Å, C—Cl⋯Cl = 152.96 (6)°].

Related literature

For charge-transfer complexes of chloranilic acid, see: Gotoh *et al.* (2006, 2007, 2008); Gotoh & Ishida (2009); Ishida (2004); Ishida & Kashino (1999). For a recent study of the formation of either salts or co-crystals by chloranilic acid with different organic bases, see: Molčanov & Kojić-Prodić (2010). For the previous determination of the title structure, see: Andersen (1967*a*) and of its hydrate, see: Andersen (1967*b*). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For a description of the Cambridge Structural Database, see: (Allen, 2002).



Experimental

Crystal data

$C_6H_2Cl_2O_4$
M_r = 208.98
Monoclinic, $P2_1/n$
a = 7.5338 (12) Å
b = 5.5225 (10) Å
c = 8.5720 (12) Å
β = 104.868 (11)°
V = 344.70 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 100 K
0.3 × 0.1 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction (2009))
T_{min} = 0.857, T_{max} = 1.000
6154 measured reflections
774 independent reflections
698 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.056
S = 1.09
774 reflections
59 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O3^{i}	0.82 (2)	2.00 (2)	2.7516 (15)	152 (2)

Symmetry code: (i) $-x+\frac{5}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO* program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2017).

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supporting information

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Chloranilic acid: a redetermination at 100 K

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S1. Comment

The crystal structures of various charge-transfer complexes of chloranilic acid have been reported (Gotoh, Asaji *et al.*, 2008; Gotoh, Asaji *et al.*, 2007; Gotoh & Ishida, 2009; Gotoh, Ishikawa, *et al.*, 2006; Ishida, 2004; Ishida & Kashino, 1999). Very recently, a study on the formation of either salts or co-crystals by chloranilic acid with the different organic bases was published (Molčanov & Kojić-Prodić, 2010).

There is a number of structures in the Cambridge Database (Allen, 2002) that contain the chloranilic acid (2,5-di-chloro-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione, **I** - Scheme 1), either as a neutral molecule or as an anion (mono- or di-). Interestingly, the only determination of the structure of the acid itself dates back to 1967 (Andersen, 1967a; hereinafter referred to as KA67). The structure was refined based on the visually estimated intensities of the diffraction spots obtained by means of the Weissenberg equi-inclination method. The quality of this structure is excellent taking into account the technology involved, but - having in mind the importance of this small molecule - thanks to the advancement of the methodology it might be desirable to get the more accurate results. Here we report the results of the structure determination of (**I**) at 100 (1) K. The unit cell parameters of the accompanying room temperature experiment are in an excellent agreement with the data of KA67, but the model is much better, for instance in terms of R factors (8.9% in 1967, with 22 reflections omitted *vs.* 2.5% in the present determination), the only symmetry independent hydrogen atom was found in the difference Fourier map in KA67 and left in the position found, while now it was isotropicaly refined, etc. Nevertheless, the basic features of the structure are similar, and both the precision and depth of the analysis in KA67 and accompanying paper on the hydrate (Andersen, 1967b) are really remarkable.

We have chosen to describe the structure in the $P2_1/n$ space group instead of $P2_1/a$ used in KA67, in order to have smaller β angle (104.87° instead of 122.77°); the transformation matrix is {-1 0 -1 0 1 0 1 0 0}. The molecule of **I** lies in the special position, across the center of symmetry (Z′=1/2). The whole molecule is planar (Fig. 1); the maximum deviation form the mean plane through 6 ring atom is 0.0014 (9) Å for the ring atom and 0.029 (3)Å for the other atoms. The bond length pattern confirms the dominant double-bond character for the bonds C3—O3 (1.224 (2) Å) and C1—C2 (1.349 (2) Å) and single-bond for C2—C3 (1.507 (2) Å) and - to the lesser extent - for C1—C3′ (1.450 (2) Å).

In the crystal structure the main packing motif arises as the result of relatively strong intermolecular O—H···O hydrogen bonds, which make the antiparallel chains of molecules related by the 2_1 screw along y direction; using the graph-set notation (Bernstein *et al.*, 1995), these first-order chains will be described as C(5). The neighboring chains are interconnected to give the centrosymmetric second-order rings R44(22) - cf. Fig. 2. These structures produce the one-molecule thick layers of molecules which expand along [101] direction, and the neighboring chains are connected by means of van der Waals interactions and probably also by weak halogen bonds, with Cl···Cl distance of 3.2838 (8)Å and C—Cl···Cl angle of 152.96 (6)° - Fig. 3.

S2. Experimental

Chloranilic acid was purchased from Loba Chemie, Mumbai, India. X-ray quality crystals were obtained from methanol solution after slow evaporation.

S3. Refinement

The position of the hydrogen atom was found in the difference Fourier map and both the positional and isotropic thermal parameters weres freely refined.

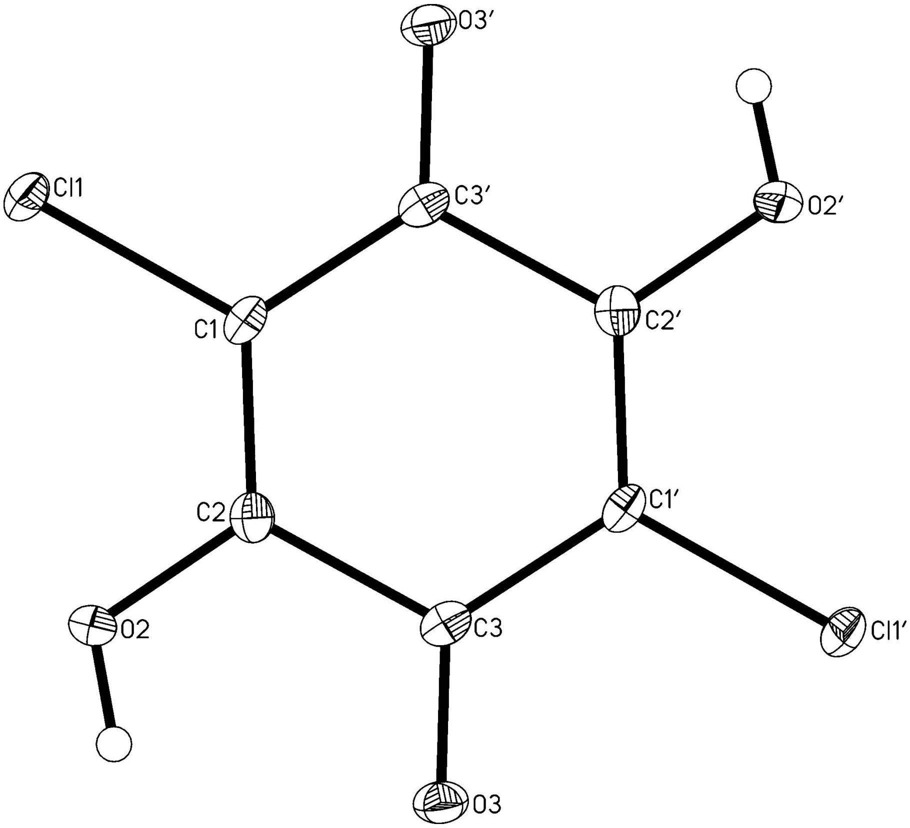

Figure 1

Anisotropic ellipsoid representation of the compound **I** together with atom labelling scheme. The ellipsoids are drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii.

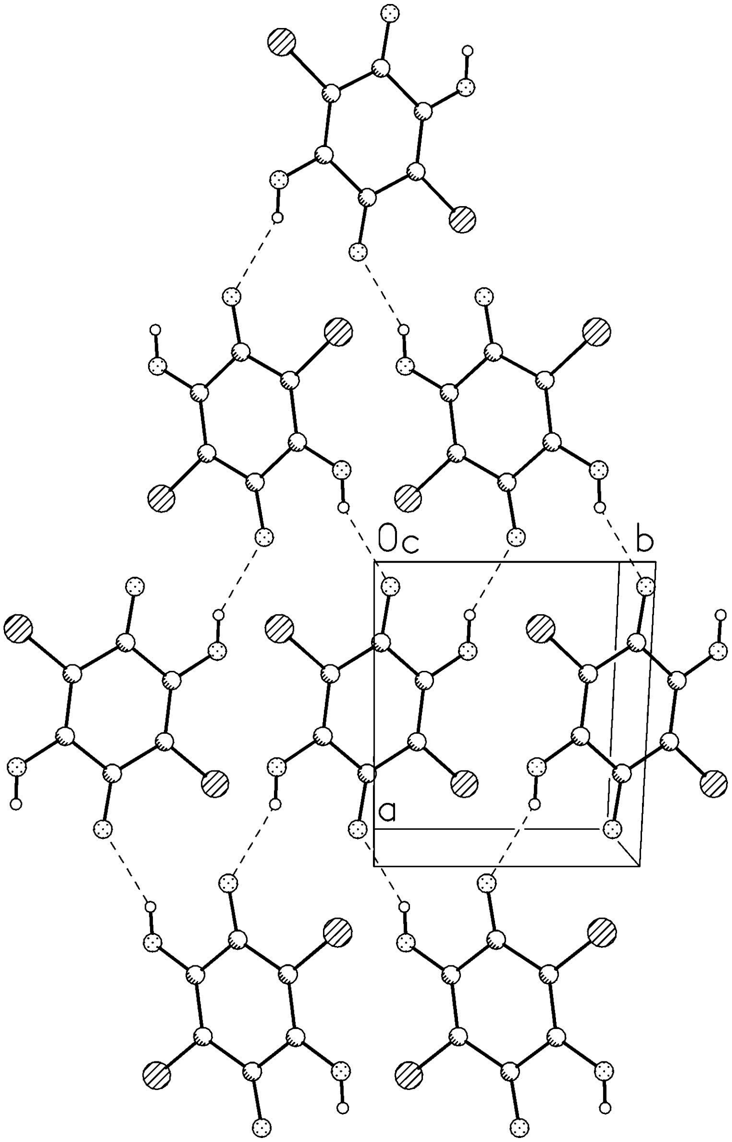

Figure 2

The hydrogen bonded motifs in the crystal structure of **I**. Hydrogen bonds are shown as dashed lines. (a) the N—H···N chain. Symmetry codex: (i) x,y,z; (ii) x,-3/2+y,3/2-z; (iii) 2-x,1/2+y,3/2-z; (iv) 2-x,-1/2+y,3/2-z; (v) 2-x,-3/2+y,3.2-z. (b) the N—H···O chains and rings. Symetry codes: (i) x,y,z; (ii) 1-x,1/2+y,3/2-z; (iii) 1-x,-1/2+y,3/2-z.

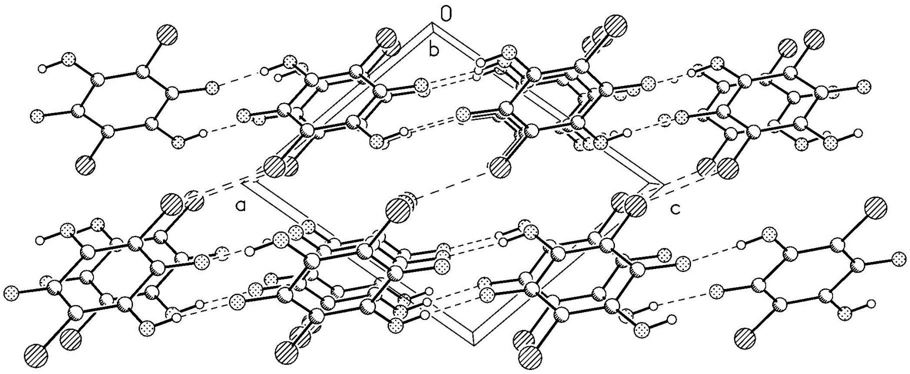

Figure 3

Crystal packing as seen along y-direction. Hydrogen bonds and Cl···Cl contacts are shown as dashed lines.

Chloranilic acid

Crystal data

$C_6H_2Cl_2O_4$
$M_r = 208.98$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.5338$ (12) Å
$b = 5.5225$ (10) Å
$c = 8.5720$ (12) Å
$\beta = 104.868$ (11)°
$V = 344.70$ (10) Å^3
$Z = 2$
$F(000) = 208$
$D_x = 2.014$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4539 reflections
$\theta = 2.8$–27.8°
$\mu = 0.90$ mm^{-1}
$T = 100$ K
Prism, red
0.3 × 0.1 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1544 pixels mm^{-1}
ω–scan
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction (2009))
$T_{min} = 0.857$, $T_{max} = 1.000$
6154 measured reflections
774 independent reflections
698 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.9°$, $\theta_{min} = 3.2°$
$h = -9 \rightarrow 9$
$k = -7 \rightarrow 7$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.056$
$S = 1.09$
774 reflections
59 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 0.3502P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
C1	0.8496 (2)	−0.1699 (3)	0.47066 (18)	0.0102 (3)
Cl1	0.66487 (5)	−0.36207 (7)	0.44138 (4)	0.01295 (13)
C2	0.9798 (2)	−0.1990 (3)	0.38967 (18)	0.0101 (3)
O2	0.97189 (15)	−0.3741 (2)	0.28296 (13)	0.0132 (3)
H2	1.064 (3)	−0.381 (4)	0.249 (3)	0.034 (7)*
C3	1.14042 (19)	−0.0274 (3)	0.41584 (17)	0.0095 (3)
O3	1.25301 (15)	−0.0641 (2)	0.33789 (13)	0.0126 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0081 (7)	0.0100 (8)	0.0122 (7)	−0.0022 (6)	0.0020 (6)	0.0014 (6)
Cl1	0.01094 (19)	0.0138 (2)	0.0150 (2)	−0.00495 (14)	0.00488 (13)	−0.00150 (14)
C2	0.0113 (7)	0.0081 (7)	0.0102 (7)	0.0005 (6)	0.0016 (6)	0.0013 (6)
O2	0.0121 (5)	0.0133 (6)	0.0163 (6)	−0.0014 (4)	0.0075 (5)	−0.0045 (4)
C3	0.0084 (7)	0.0103 (7)	0.0098 (7)	0.0010 (6)	0.0021 (6)	0.0041 (6)
O3	0.0121 (5)	0.0131 (6)	0.0147 (5)	0.0003 (4)	0.0072 (4)	0.0008 (4)

Geometric parameters (Å, º)

C1—C2	1.349 (2)	C2—C3	1.508 (2)
C1—C3^{i}	1.450 (2)	O2—H2	0.82 (2)
C1—Cl1	1.7164 (15)	C3—O3	1.2240 (18)
C2—O2	1.3217 (19)		
C2—C1—C3^{i}	121.02 (14)	C1—C2—C3	120.71 (14)
C2—C1—Cl1	121.38 (12)	C2—O2—H2	112.9 (17)
C3^{i}—C1—Cl1	117.59 (11)	O3—C3—C1^{i}	124.53 (14)
O2—C2—C1	122.23 (14)	O3—C3—C2	117.19 (14)
O2—C2—C3	117.05 (13)	C1^{i}—C3—C2	118.27 (13)
C3^{i}—C1—C2—O2	−178.48 (14)	O2—C2—C3—O3	−0.8 (2)
Cl1—C1—C2—O2	0.7 (2)	C1—C2—C3—O3	−179.74 (14)

C3^{i}—C1—C2—C3	0.4 (2)	O2—C2—C3—C1^{i}	178.55 (13)
Cl1—C1—C2—C3	179.51 (11)	C1—C2—C3—C1^{i}	−0.4 (2)

Symmetry code: (i) −*x*+2, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3^{ii}	0.82 (2)	2.00 (2)	2.7516 (15)	152 (2)

Symmetry code: (ii) −*x*+5/2, *y*−1/2, −*z*+1/2.