Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen bonding in 1,2-diazine–chloranilic acid (2/1) and 1,4-diazine–chloranilic acid (2/1) determined at 110 K

Kazuma Gotoh,[a] Tetsuo Asaji[b] and Hiroyuki Ishida[a]*

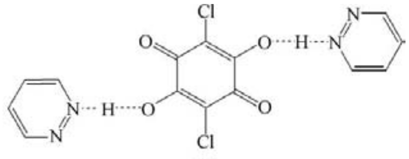
[a]Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan, and [b]Department of Chemistry, College of Humanities and Sciences, Nihon University, Tokyo 156-8550, Japan
Correspondence e-mail: ishidah@cc.okayama-u.ac.jp

Received 1 September 2008
Accepted 10 September 2008
Online 20 September 2008

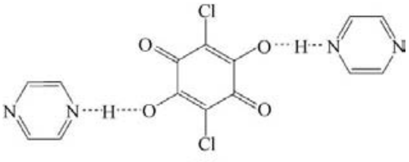
The crystal structures of the isomeric title compounds [systematic names: pyridazine–2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone (2/1), (I), and pyrazine–2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone (2/1), (II)], $2C_4H_4N_2 \cdot C_6H_2Cl_2O_4$, have been redetermined at 110 K. The H atom in the intermolecular O···H···N hydrogen bond in each compound was revealed to be disordered; the relative occupancies at the O and N sites are 0.33 (3) and 0.67 (3), respectively, for (I), and 0.56 (4) and 0.44 (4) for (II). The formal charges of the chloranilic acid in (I) and (II) estimated from the occupancy factors are *ca* −1.3 and −0.8, respectively. The geometries of the centrosymmetric chloranilic acid molecule in (I) and (II) are compared with the neutral, monoanionic and dianionic forms of chloranilic acid optimized by density functional theory (DFT) at the B3LYP/6–311+G(3df,2p) level. The result implies that the chloranilic acid molecule in (I) is close to the monoanionic state, while that in (II) is between neutral and monoanionic, consistent with the result derived from the H-atom occupancies.

Comment

The crystal structures of 1,2-diazine–chloranilic acid (2/1), (I), and 1,4-diazine–chloranilic acid (2/1), (II), have already been determined at room temperature (Ishida & Kashino, 1999*a*,*b*). In each compound, the diazine and chloranilic acid molecules are connected by strong N···H···O hydrogen bonds [N···O = 2.582 (3) Å in (I) and 2.590 (4) Å in (II)] to afford a centrosymmetric 2:1 unit. In the hydrogen bond of (I), the H atom was found near the centre of N···O, while in (II), the H atom was located near the O-atom site with a fairly long O—H bond [O—H = 1.06 (5) Å]. From the positions of the H atoms and the large $U_{\rm iso}$(H) values [$U_{\rm iso}$(H) = 0.16 (1) Å^2 for (I) and 0.12 (1) Å^2 for (II)], disorder of the H atoms in the hydrogen bonds was suggested. Proton motion attributable to dynamically disordered H atoms in the hydrogen bonds was detected by ^{1}H NMR and ^{35}Cl NQR measurements for (I) (Nihei *et al.*, 2000*a*) and (II) (Nihei *et al.*, 2000*b*). The proton-transfer modes shown in Fig. 1 were proposed and the corresponding activation energies were estimated.



(I)



(II)

Interestingly, (I) showed an anomalous positive temperature coefficient of ^{35}Cl NQR resonance frequencies on heating in the range 77–170 K, which cannot be explained by the conventional Bayer-type lattice motion (Bayer, 1951). On the other hand, (II) showed a normal negative temperature coefficient of ^{35}Cl NQR frequencies. The anomalous behaviour of (I) has been interpreted (Nihei *et al.*, 2000*a*) by population changes of chloranilate(2−) and hydrogen chloranilate(1−) ions with temperature. The population of chloranilate(2−) ions decreases on heating from 77 K, while that of hydrogen chloranilate(1−) ions increases. In other words, the H atom in the N···H···O hydrogen bond migrates from the N-atom site to the O-atom site with increasing temperature. However, no crystallographic evidence has been obtained yet.

Recently, Suzuki *et al.* (2007) measured IR absorption spectra and dielectric responses of (I) over a wide temperature

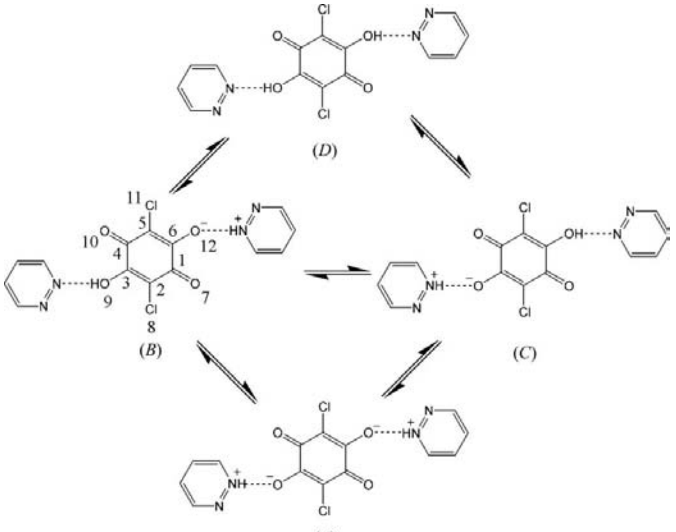


Figure 1
Proton-transfer models proposed for (I) and the numbering scheme of the hydrogen chloranilate monoanion in (*B*) used for the DFT calculations.

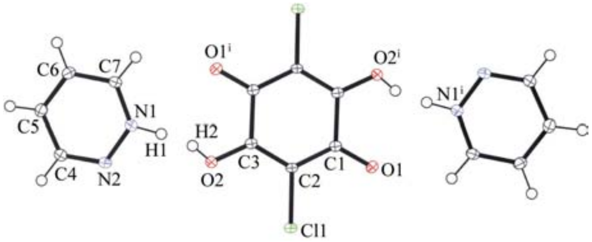


Figure 2

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.]

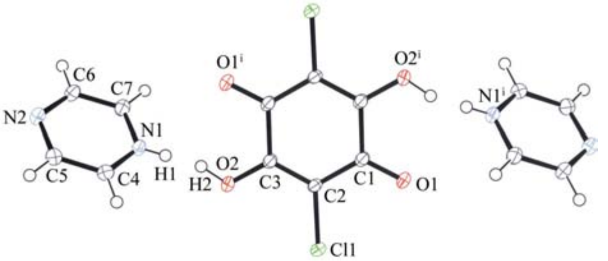


Figure 3

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 2, -y, -z + 1$.]

range. These authors observed O—H stretching and bending, C—O stretching and N—H stretching bands in IR spectra, and a broad maximum around 120 K in dielectric response. The first three IR bands were found to increase as the temperature was lowered, while the last band decreases. The authors therefore interpreted the broad maximum in dielectric response in terms of H-atom migration from N—H···O at 300 K to N···H—O below 90 K, which contradicts the interpretation from NQR.

In the present study, we collected single-crystal X-ray diffraction data at low temperature in order to clarify the hydrogen-bond states in both compounds. Wilson and co-workers have recently shown that high-quality X-ray diffraction data can be used to elucidate the relative site occupancies of the H atom in hydrogen-bond systems (Wilson & Goeta, 2004; Parkin *et al.*, 2004). This prompted us to redetermine the crystal structures of the title compounds with relatively high-redundancy data at 110 K. The weak intermolecular interactions and crystal packing, which were unclear in the previous study at room temperature, are of additional interest.

The molecular structures of (I) and (II) are shown in Figs. 2 and 3, respectively. Although the structures are essentially the same as those at room temperature (Ishida & Kashino, 1999*a*,*b*), two disordered positions of the H atom in the hydrogen bond were clearly found in the difference Fourier map in each compound. The positional parameters and the occupancy factors were refined, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(N or O). The refined occupancy factors at the O and N sites are 0.33 (3) and 0.67 (3), respectively, for (I), and 0.56 (4) and 0.44 (4) for (II). The occupancies at the O and N sites as estimated from the peak heights in the difference Fourier maps are 0.35 (1) and 0.65 (1), respectively, for (I), and 0.58 (1) and 0.42 (1) for (II). Therefore, the formal charges of the chloranilic acid molecules in (I) and (II) are *ca* −1.3 and −0.8, respectively.

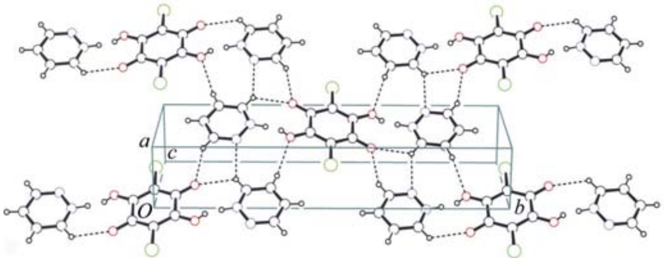


Figure 4

A packing diagram for (I), showing a molecular sheet formed by C—H···N and C—H···O hydrogen bonds (dashed lines).

A difference in the charge state between (I) and (II) was also found in the molecular geometries of chloranilic acid. In Table 3, the C—C, C—O and C—Cl bond lengths of chloranilic acid in (I) and (II) are given, together with calculated values for the neutral, monoanionic and dianionic forms of chloranilic acid. The calculation was carried out at the B3LYP/6-311+G(3df,2p) level of theory using the computer program *GAUSSIAN98* (Frisch *et al.*, 1998). Although the monoanion is noncentrosymmetric, the average structure of states (*B*) and (*C*) shown in Fig. 1 is centrosymmetric, if a rapid exchange between these states is assumed. In Table 3, the bond lengths of the average structure of the monoanionic state are given. The geometries corresponding to the (*B*) state are given in the footnote of Table 3. The C2—C3, C1—C3$^{\rm i}$ [symmetry code (i) given in Table 3], C1—O1 and C2—Cl1 bonds of (I) are longer than those of (II), while the C1—C2 and C3—O2 bonds of (I) are shorter than those of (II). The calculated data show that the former bond lengths increase in the order neutral < monoanionic < dianionic state, while the latter bonds decrease in the order neutral > monoanionic > dianionic state. This implies that the chloranilic acid in (I) has a more negative charge than that in (II). The geometries of chloranilic acid in (I) are close to the monoanionic state, while (II) has intermediate values between the neutral and monoanionic states, which are consistent with the formal charges estimated from the occupancy factors of the H atoms.

In the crystal structure of (I), the 1,2-diazine–chloranilic acid (2/1) unit is approximately planar, with a dihedral angle of 14.32 (5)° between the diazine ring and the chloranilic acid C1–C3/C1$^{\rm i}$–C3$^{\rm i}$ plane [symmetry code (i) given in Table 1]. The 2:1 units are connected by C—H···O and C—H···N hydrogen bonds, forming a molecular sheet extending parallel to the $(\bar{1}02)$ plane (Fig. 4). In (II), the 2:1 unit is considerably twisted, with a dihedral angle of 52.35 (6)° between the diazine and chloranilic acid planes. The units are linked by weak C—H···O hydrogen bonds (Table 2), forming a molecular sheet parallel to the (010) plane (Fig. 5). No C—H···N hydrogen bond exists in (II), but a Cl1···N2 short contact [3.1520 (15) Å] is observed in the sheet.

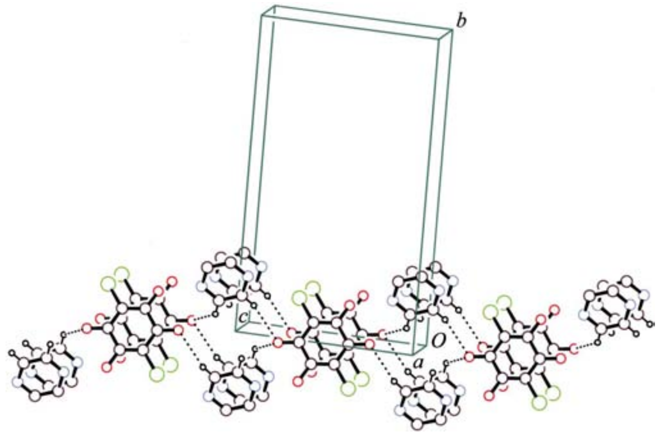


Figure 5
A partial packing diagram for (II), viewed approximately down the *a* axis, showing a molecular sheet formed by weak C—H···O hydrogen bonds (dashed lines). H atoms not involved in these hydrogen bonds have been omitted for clarity.

In this communication, we can clearly show the disordered states of the H atoms in both compounds. Although the relative occupancy factors evaluated for (I) imply a double-well hydrogen bond with a lower potential energy at the N site and support the interpretation from the NQR data, *i.e.* proton migration from the N site to the O site with increasing temperature, more detailed experiments are required to confirm it. Multitemperature X-ray diffraction measurements with ^{14}N NQR experiments are in progress for (I) to clarify the charge states of both chloranilic acid and 1,2-diazine.

Experimental

Single crystals of (I) were obtained by slow evaporation from a methanol solution (100 ml) of chloranilic acid (0.197 g) and 1,2-diazine (0.155 g) at room temperature. Crystals of (II) were obtained by slow evaporation from an acetonitrile solution (150 ml) of chloranilic acid (0.209 g) and 1,4-diazine (0.165 g) at room temperature.

Compound (I)

Crystal data

$2C_4H_4N_2 \cdot C_6H_2Cl_2O_4$
$M_r = 369.16$
Monoclinic, $P2_1/c$
$a = 3.72940$ (13) Å
$b = 20.0950$ (5) Å
$c = 9.6217$ (2) Å
$\beta = 98.8484$ (11)°
$V = 712.49$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.48$ mm^{-1}
$T = 110$ (1) K
0.35 × 0.25 × 0.10 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Absorption correction: numerical (*ABSCOR*; Higashi, 1999)
$T_{\min} = 0.868$, $T_{\max} = 0.953$
11510 measured reflections
2070 independent reflections
1883 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.084$
$S = 1.08$
2070 reflections
116 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1$^{\rm i}$	0.71 (5)	2.32 (4)	2.6831 (11)	114 (4)
O2—H2···N1	0.71 (5)	1.89 (5)	2.5549 (12)	156 (5)
N1—H1···O1$^{\rm i}$	0.91 (2)	2.46 (2)	2.9641 (12)	115.5 (17)
N1—H1···O2	0.91 (2)	1.66 (2)	2.5549 (12)	165 (2)
C4—H4···O1$^{\rm ii}$	0.95	2.36	3.2251 (14)	152
C6—H6···O2$^{\rm iii}$	0.95	2.47	3.3769 (14)	161
C7—H7···O1$^{\rm i}$	0.95	2.35	2.9579 (13)	121
C7—H7···N2$^{\rm iii}$	0.95	2.57	3.3548 (15)	141

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

Compound (II)

Crystal data

$2C_4H_4N_2 \cdot C_6H_2Cl_2O_4$
$M_r = 369.16$
Monoclinic, $P2_1/n$
$a = 3.7530$ (3) Å
$b = 18.3915$ (14) Å
$c = 10.7248$ (8) Å
$\beta = 94.103$ (3)°
$V = 738.36$ (10) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.47$ mm^{-1}
$T = 110$ (1) K
0.40 × 0.18 × 0.10 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1999)
$T_{\min} = 0.845$, $T_{\max} = 0.954$
14174 measured reflections
2154 independent reflections
1929 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.108$
$S = 1.03$
2154 reflections
116 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1$^{\rm i}$	0.86 (5)	2.33 (5)	2.7038 (16)	107 (3)
O2—H2···N1	0.86 (5)	1.73 (5)	2.5576 (18)	163 (4)
N1—H1···O1$^{\rm i}$	0.74 (6)	2.53 (5)	2.9044 (18)	113 (5)
N1—H1···O2	0.74 (6)	1.83 (6)	2.5576 (18)	171 (6)
C6—H6···O1$^{\rm ii}$	0.95	2.59	3.505 (2)	162
C7—H7···O1$^{\rm iii}$	0.95	2.59	3.303 (2)	132

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

For both compounds, H atoms in the N···H···O hydrogen bonds were found to be disordered in difference Fourier maps. Since the site-occupancy factors and isotropic displacement parameters were strongly correlated, the positional parameters and occupancy factors were refined, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(N or O). The refined distances are given in Tables 1 and 2. Other H atoms were positioned geometrically (C—H = 0.95 Å) and treated as riding, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). The *ab initio* molecular calculations were performed using *GAUSSIAN98* (Frisch *et al.*, 1998) at the B3LYP/6-311+G(3df,2p) (Becke, 1993; Lee *et al.*, 1988) level of theory. The full optimizations were carried out for chloranilic acid, the hydrogen chloranilate

o552 Gotoh *et al.* • Two isomers of $2C_4H_4N_2 \cdot C_6H_2Cl_2O_4$ *Acta Cryst.* (2008). C**64**, o550–o553

Table 3
Selected geometric parameters (Å) of chloranilic acid observed in (I) and (II), and calculated (DFT) data for neutral chloranilic acid, the hydrogen chloranilate monoanion and the chloranilate dianion.

	(I)	(II)	Neutral	Monoanion†	Dianion
C1—C2	1.4271 (14)	1.444 (2)	1.4510	1.4229	1.4131
C2—C3	1.3802 (14)	1.362 (2)	1.3508	1.3869	1.4131
C1—C3^{i}	1.5373 (15)	1.520 (2)	1.5166	1.5514	1.5786
C1—O1	1.2355 (13)	1.2266 (18)	1.2179	1.2329	1.2365
C3—O2	1.2741 (13)	1.3005 (19)	1.3185	1.2722	1.2365
C2—Cl1	1.7373 (11)	1.7211 (15)	1.7178	1.7462	1.7853

† The average value of two bond lengths, which would be related by an inversion centre in the cases of the neutral and dianionic states. The calculated bond lengths for the monoanionic state (*B*) as shown in Fig. 1 are 1–2 = 1.4575, 2–3 = 1.3478, 3–4 = 1.5210, 4–5 = 1.3882, 5–6 = 1.4259, 1–6 = 1.5817, 1–7 = 1.2115, 4–10 = 1.2543, 3–9 = 1.3224, 6–12 = 1.2220, 2–8 = 1.7440 and 5–11 = 1.7483 Å. Symmetry codes: (i) $-x+2, -y+1, -z+1$, for (I); (i) $-x+2, -y, -z+1$, for (II).

monoanion and the chloranilate dianion, and the resultant stable structures were confirmed by the vibrational analysis, which shows only real frequencies for the optimized structures.

For both compounds, data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 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).

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 19550018) from the Japan Society for the Promotion of Science.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3243). Services for accessing these data are described at the back of the journal.

References

Bayer, H. (1951). *Z. Phys.* **130**, 227–238.

Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Frisch, M. J. *et al.* (1998). *GAUSSIAN98*. Revision A7. Gaussian Inc., Pittsburgh, Pennsylvania, USA.

Higashi, T. (1999). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Ishida, H. & Kashino, S. (1999*a*). *Acta Cryst.* C**55**, 1149–1152.

Ishida, H. & Kashino, S. (1999*b*). *Acta Cryst.* C**55**, 1714–1717.

Lee, C., Yang, W. & Parr, R. G. (1988). *Phys. Rev.* B**37**, 785–789.

Nihei, T., Ishimaru, S., Ishida, H., Ishihara, H. & Ikeda, R. (2000*a*). *Chem. Lett.* **29**, 1346–1347.

Nihei, T., Ishimaru, S., Ishida, H., Ishihara, H. & Ikeda, R. (2000*b*). *Chem. Phys. Lett.* **329**, 7–14.

Parkin, A., Harte, S. M., Goeta, A. E. & Wilson, C. C. (2004). *New J. Chem.* **28**, 718–721.

Rigaku/MSC (2004). *PROCESS-AUTO* and *CrystalStructure* (Version 3.7.0). Rigaku/MSC, The Woodlands, Texas, USA.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Suzuki, H., Mori, H., Yamaura, J., Matsuda, M., Tajima, H. & Mochida, T. (2007). *Chem. Lett.* pp. 402–403.

Wilson, C. C. & Goeta, A. E. (2004). *Angew. Chem. Int. Ed.* **43**, 2095–2099.