
Okayama University *Year* 2007

Hydrogen bonding in two solid phases of phenazine-chloranilic acid (1/1) determined at 170 and 93 K

Kazuma Gotoh* Tetsuo Asaji†
Hiroyuki Ishida‡

*Okayama University, kgotoh@cc.okayama-u.ac.jp
†Nihon University
‡Okayama University

http://escholarship.lib.okayama-u.ac.jp/crystallography/1

19 Nov 2006

Hydrogen bonding in two solid phases of phenazine-chloranilic acid (1/1) determined at 170 and 93 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, Graduate School of Integrated Basic Sciences, College of Humanities and Sciences, Nihon University, Tokyo 156-8550, Japan. E-mail: ishidah@cc.okayama-u.ac.jp*

Abstract

The crystal structures in two solid phases, *i.e.*, phase II stable between 146 and 253 K and phase IV below 136 K, of the title compound ($C_{12}H_8N_2.C_6H_2Cl_2O_4$ in phase II and $C_{12}H_9N_2^+.C_6HCl_2O_4^-$ in phase IV), have been determined. The crystal in both phases crystallizes in $P2_1$ and the structure was refined as an inversion twin. In phase II, the phenazine and chloranilic acid molecules are arranged alternately through two kinds of O—H···N hydrogen bonds. In phase IV, salt formation occurs by donation of one H atom from chloranilic acid to the phenazine molecule; the resulting monocation and monoanion are linked by N—H···O and O—H···N hydrogen bonds.

Comment

Chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone), a strong dibasic acid with hydrogen-bond donor as well as acceptor groups, appears particularly attractive as a template for generating tightly bound self-assemblies with various pyridine derivatives (Ishida & Kashino, 1999*a*,*b*,*c*, 2002; Zaman *et al.*, 1999, 2000; Akhtaruzzaman *et al.*, 2001; Ishida, 2004*a*,*b*,*c*; Tabuchi *et al.*, 2005) as well as a model compound for investigating hydrogen transfer motions in O—H···N and N—H···O hydrogen bond systems (Nihei *et al.*, 2000*a*,*b*; Ikeda *et al.*, 2005). Recently, it has been revealed by Horiuchi, Ishii *et al.* (2005) that the title compound, consisting of non-polar $C_{12}H_8N_2$ and $C_6H_2O_4Cl_2$ molecules held together through O—H···N hydrogen bonds, has a ferroelectric phase (designated as phase II) below 253 K. The compound in phase II crystallizes in $P2_1$, while it is $P2_1/n$ in the room temperature phase (phase I). Horiuchi, Kumai *et al.* (2005) have also found that the transition temperature is elevated by 51 K for phazine–deuterated chloranilic acid (1/1), $C_{12}H_8N_2.C_6D_2Cl_2O_4$, indicating the significant effect of the hydrogen bonding on the phase transition. In these phases, we have measured the temperature dependence of ^{35}Cl nuclear quadrupole resonance (NQR) frequencies and spin-lattice relaxation time T_1 (Asaji *et al.*, 2006). The single NQR line observed in phase I is consistent with the reported crystal structure in space group $P2_1/n$. The line splits into a doublet below the transition point (the resonance frequencies are 36.880 and 36.750 MHz at 209 K), indicating that the chloranilic acid has lost its centre of symmetry and that the two Cl atoms in the chloranilic acid are inequivalent in phase II. This observation excludes the centrosymmetric space group $P2_1/n$ in phase II and is consistent with the space group $P2_1$ proposed for the ferroelectric phase of the compound. The two N atoms of the phenazine molecule in phase II have also been found to be inequivalent by ^{14}N NQR measurements (Seliger, 2006). Furthermore, the existence of a hydrogen transfer motion in the hydrogen bond was suggested from the ^{35}Cl NQR T_1 measurements.

Very recently, heat capacity measurements by Saito *et al.* (2006) have indicated new phase transitions at 136 and 146 K: these have also been detected in phenazine–deuterated chloranilic acid by our NQR measurements (Watanabe *et al.*, 2006). With decreasing temperature, the two NQR lines in phase II disappear around 200 K and then another two lines appear below 160 K. The temperatures at which the NQR signals fade out and re-appear can be assigned to the transition points corresponding to those observed by heat capacity measurements, taking into account the effect of deuteration on the transition temperatures. In the lowest-temperature phase, one of the two NQR lines (36.77 and 36.16 MHz at 95 K) appears with a remarkable shift to lower frequency compared with the two lines in phase II, implying that the charge state of the chloranilic acid changes from neutral in phase II to monovalent cation (##AUTHOR: do you mean a singly charged anion?)

in the lowest temperature phase (Hart *et al.*, 1972). In the present study, we have determined the structure of the newly discovered low-temperature phase (designated as phase IV) at 93 K and re-determined the structure of the ferroelectric phase (phase II) at 170 K in order to clarify the hydrogen bonding scheme in each phase.

The crystal in phase II was treated as an inversion twin and the refined structure (Fig. 1) is consistent with that reported by Horiuchi, Ishii *et al.* (2005), but more precise molecular geometries were obtained (Table 1). The chloranilic acid molecule shows a characteristic structure, having four short C—C bonds [1.3547 (17)–1.4583 (15) Å] and two extremely long C—C bonds [1.5115 (18)–1.5251 (18) Å], which is explainable in terms of the double π system of the anion (Anderson, 1967*c*; Benchekroun & Savariault, 1995). In the crystal, the phenazine and chloranilic acid molecules are arranged alternately through two kinds of O—H···N hydrogen bonds (Table 2) to form a supramolecular chain running along the [110] direction (Fig. 2). Intermolecular C—H···O and intramolecular O—H···O hydrogen bonds are also observed in the chain structure. The phenazine and chloranilic acid planes are considerably twisted, the dihedral angle between them being 44.51 (4)°. The chains related by translation along the *b* axis are stacked together by π-π interactions to form a molecular layer extending parallel to the (001) plane. The interplanar distance between π-π interacting phenazine planes is 3.360 (11) Å. It is interesting to note that the H atom (H4) involved in the shorter O—H···N hydrogen bond (O4—H4···N2) has a considerably large $U_{\rm iso}$ value [0.131 (14) Å^2] compared to that [0.047 (6) Å^2] of the other H atom (H2) involved in the longer O—H···N hydrogen bond (O2—H2···N1^i; symmetry code as in Table 2) and that the O4—H4 bond is much longer than the O2—H2 bond. These facts are explainable by a dynamic disorder of the atom H4 in the hydrogen bond, as suggested from NQR T_1 measurements (Asaji *et al.*, 2006).

Phase IV also crystallizes in the non-centrosymmetric space group $P2_1$, which is consistent with the NQR result, and it is found to be twinned by inversion. The cell dimensions *b* and *c* are somewhat shortened, while the dimension *a* is lengthened. The molecular geometries (Table 3) and the arrangement of the molecules are essentially same as those in phase II, but in phase IV the H atom corresponding to H4 in phase II was found to be bonded to N2 (##AUTHOR: please approve the preceding change), which implies that salt formation occurs by donation of one of the two H atoms from chloranilic acid to the phenazine molecule in this phase (Fig. 3). This fact is supported by the NQR result which implies the existence of the hydrogen chloranilate monoanion. The resulting phenazinium cation and hydrogen chloranilate anion are linked together by N2—H4$\cdots$O4 and O2—H2$\cdots$N1^{i} hydrogen bonds (symmetry code as in Table 4), forming a chain running along the [110] direction (Fig. 4). The O4$\cdots$N2 distance is shortened compared with that in phase II, while the O2$\cdots$N1 distance is lengthened. The dihedral angle of 44.30 (4)° between the phenazinium and chloranilate planes is almost the same as in phase II. Phenazine planes linked by π-π interactions are related by translation along the *b* axis at an interplanar distance of 3.343 (12) Å. (##AUTHOR: please approve preceding re-wording) The $U_{\rm iso}$(H) value of H4 is still rather large [0.091 (10) Å^2] and the N2—H4 bond is long, suggesting that the H4 atom is also disordered in this phase.

Typical bond lengths of C═O and C—O(—H) in neutral chloranilic acid are 1.22 (1) and 1.32 (1) Å, respectively (Andersen, 1967*a*,*b*; Zaman *et al.*, 2004) and those of C═O and C—O$^-$ in chloranilate monoanion are 1.24 (2) and 1.25 (2) Å. The values are somewhat scattered and depend on the hydrogen bonding scheme (##AUTHOR: please approve preceding re-wording) around the O atoms (Ishida & Kashino, 1999*a*, 2002; Ishida, 2004*a*; Gotoh *et al.*, 2006). In phase II, the C—O bond lengths in one π electronic system of the chloranilic acid are within the above range [C1═O1 1.2269 (15) and C3—O2(—H2) 1.3204 (13) Å; Table 1], but those in the other system [C4═O3 1.2291 (15) and C6—O4(—H4) 1.2923 (13) Å] deviate slightly from the above values (##AUTHOR: please approve preceding re-wording). Taking account of both this and the NQR results, we conclude that the chloranilic acid in phase II has a charge close to, but not exactly, zero due to the proton transfer motion of atom H4. In phase IV, the C—O bond lengths in one π electronic system of the chloranilate monoanion are 1.2259 (15) and 1.3291 (13) Å for C1═O1 and C3—O2(—H2), respectively, while those in the other system are 1.2310 (15) and 1.2901 (13) Å for C4═O3 and C6—O4$^-$ (Table 3). The C4═O3 and C6—O4 in phase IV are longer and shorter, respectively, than those in phase II, being consistent with salt formation in phase IV. The change in the C4═O3 and C6—O4 bond distances between phase II and IV is, however, rather small and the C6—O4$^-$ bond in phase IV is somewhat long compared with the typical C—O$^-$ bond. Thus, we conclude that the charge state of the chloranilate anion in phase IV is not exactly charge −1, due to the proton motion in the hydrogen bond. The difference in C—N bond lengths between phase II and IV is also small, again probably due to the proton motion, although a detectable difference can be expected from the calculated bond lengths for the isolated phenazine and the phenaziniun cation in the gas phase at the B3LYP/6–311 G(2 d,2*p*) level of theory by using the *GAUSSIAN*98 program (Frisch *et al.*, 1998); the calculated C—N bond length of phanazine is 1.3373 Å, while the C—N$^+$(—H) and C—N lengths of the protonated cation are 1.3557 and 1.3345 Å, respectively.

It is important to note that NQR measurements allow an unambiguous choice between space groups $P2_1$ and $P2_1/n$. Since the NQR frequencies are sensitive to the electronic state of the resonant nucleus, and therefore to the structural environment of that atom, NQR is a useful method for obtaining conclusive non-crystallographic evidence for the resolution of centrosymmetric/non-centrosymmetric space group ambiguity (##AUTHOR: please approve preceding re-wording).

Experimental

Single crystals suitable for X-ray diffraction were obtained by slow diffusion between a solution of chloranilic acid (0.104 g) in ethanol (10 ml) and a solution of phenazine (0.090 g) in ethanol (10 ml). (##AUTHOR: please approve preceding re-wording).

Compound II

Crystal data

$C_{12}H_8N_2.C_6H_2Cl_2O_4$	Mo $K\alpha$ radiation
$M_r = 389.19$	$\lambda = 0.71075$ Å
Monoclinic	Cell parameters from 41779 reflections
$P2_1$	$\theta = 3.3$–$40.4°$
$a = 12.4268\,(2)$ Å	$\mu = 0.457$ mm^{-1}
$b = 3.7960\,(1)$ Å	$T = 170\,(2)$ K
$c = 16.9218\,(3)$ Å	Block
$\beta = 107.812\,(1)°$	Brown
$V = 759.97\,(3)$ Å^3	0.40 × 0.25 × 0.25 mm
$Z = 2$	
$D_x = 1.701$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku RAXIS–RAPID image plate diffractometer

ω scans

Absorption correction:
multi-scan (*ABSCOR*; Higashi, 1995).
$T_{\min} = 0.766$, $T_{\max} = 0.892$

46939 measured reflections

9059 independent reflections

7499 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.0517$

$\theta_{\max} = 40.23°$

$h = -22 \rightarrow 22$

$k = -6 \rightarrow 6$

$l = -30 \rightarrow 30$
every 0. reflections
frequency: 0. min

Refinement

Refinement on F^2

$R(F) = 0.0339$

$wR(F^2) = 0.0965$

$S = 1.059$

9059 reflections

245 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.1226P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.562$ e Å^{-3}

$\Delta\rho_{\min} = -0.378$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Absolute structure: Flack (1983); 3778 Friedel pairs

Flack parameter = 0.48 (5)

Table 1. *Selected geometric parameters (Å, °) for II*

Cl1—C2	1.7206 (12)	O4—C6	1.2923 (13)
Cl2—C5	1.7217 (12)	N1—C12	1.3503 (17)
O1—C1	1.2269 (15)	N1—C17	1.3442 (14)
O2—C3	1.3204 (13)	N2—C11	1.3493 (13)
O3—C4	1.2291 (15)	N2—C18	1.3472 (17)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O3	0.73 (2)	2.32 (2)	2.6809 (13)	113 (2)
O2—H2$\cdots$N1$^{\text{i}}$	0.73 (2)	2.15 (2)	2.7722 (16)	145 (2)
O4—H4$\cdots$N2	1.02 (4)	1.66 (4)	2.6446 (16)	159 (3)
C7—H7$\cdots$O2$^{\text{ii}}$	0.95	2.56	3.2668 (19)	131
C10—H10$\cdots$O1	0.95	2.57	3.3153 (15)	136
C13—H13$\cdots$O4	0.95	2.57	3.2283 (19)	127

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

Compound IV

Crystal data

$C_{12}H_9N_2^+.C_6HCl_2O_4^-$

$M_r = 389.19$

Monoclinic

$P2_1$

$a = 12.4320\ (3)$ Å

$b = 3.7702\ (1)$ Å

$c = 16.8848\ (4)$ Å

$\beta = 107.778\ (1)^\circ$

$V = 753.62\ (3)$ Å^3

$Z = 2$

$D_x = 1.715$ Mg m^{-3}

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71075$ Å

Cell parameters from 36807 reflections

$\theta = 3.3$–40.4°

$\mu = 0.461$ mm^{-1}

$T = 93\ (2)$ K

Block

Brown

0.40 × 0.25 × 0.25 mm

Data collection

Rigaku RAXIS–RAPID image plate diffractometer

ω scans

Absorption correction:
multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.759$, $T_{\max} = 0.891$

44236 measured reflections

8923 independent reflections

7463 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0373$

$\theta_{\max} = 40.25^\circ$

$h = -22 \rightarrow 22$

$k = -6 \rightarrow 6$

$l = -30 \rightarrow 30$
every 0. reflections
frequency: 0. min

Refinement

Refinement on F^2

$R(F) = 0.0323$

$wR(F^2) = 0.0885$

$S = 1.059$

8923 reflections

245 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.1204P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.537$ e Å^{-3}

$\Delta\rho_{\min} = -0.437$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Absolute structure: Flack (1983); 3684 Friedel pairs

Flack parameter = 0.51 (4)

Table 3. *Selected geometric parameters (Å, °) for IV*

Cl1—C2	1.7203 (12)	O4—C6	1.2901 (13)
Cl2—C5	1.7229 (12)	N1—C12	1.3502 (15)
O1—C1	1.2259 (15)	N1—C17	1.3467 (13)
O2—C3	1.3191 (13)	N2—C11	1.3487 (13)
O3—C4	1.2310 (15)	N2—C18	1.3466 (16)

Table 4. *Hydrogen-bonding geometry (Å, °) for IV*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O3	0.79 (2)	2.31 (2)	2.6758 (13)	109.5 (19)
O2—H2$\cdots$N1^{i}	0.79 (2)	2.08 (2)	2.7739 (15)	146 (2)
N2—H4$\cdots$O4	1.12 (3)	1.57 (3)	2.6368 (16)	158 (3)
C7—H7$\cdots$O2^{ii}	0.95	2.56	3.2619 (19)	131
C10—H10$\cdots$O1	0.95	2.56	3.3095 (15)	136
C13—H13$\cdots$O4	0.95	2.56	3.2211 (19)	127

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

For both phase II and IV, H atoms attached to O and N atoms were found in a difference Fourier map and refined isotropically. Refined distances are given in Table 2 and 4. Other H atoms are treated as riding, with C—H = 0.95 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The present refinement gives a slightly better result than the refinement with the distance restraint [O—H = 0.82 (1) or N—H = 0.87 Å] in terms of the residual electron densities around N and O atoms.

Crystals in phase II and IV are monoclinic; the systematic absences suggested $P2_1$ and $P2_1/m$ as possible space groups. The structures could be solved in space group $P2_1$ but not in $P2_1/m$. Analysis of the refined structures by *PLATON* (Spek, 2003) showed pseudo-symmetry ($P2_1/n$) and we confirmed that refinements in both $P2_1$ and $P2_1/n$ led to satisfactory structures in both phases. However, the ferroelectricity in phase II and the detection by ^{35}Cl NQR of two inequivalent Cl atoms in phase II and IV exclude the space group $P2_1/n$. Moreover, a number of $h0l$ reflections with $h+l = 2n+1$ at the $I > 3\sigma(I)$ level were observed [*ca* 750 reflections with $I > 3\sigma(I)$ of *ca* 3000 measured $h0l$ reflections with $h+l = 2n+1$ in both phases], although the observed number and the average intensity are smaller than those of $h0l$ reflections with $h+l = 2n$. Thus, we have selected $P2_1$ as the space group for phase II and IV. The Flack parameters for phase II and IV before the final refinement are 0.48 (5) and 0.51 (4), respectively, implying that the crystal in both phases is racemic. The final structural model was refined as an inversion twin, resulting in almost equal populations [0.52 (5)/0.48(5) for phase II and 0.49 (4)/0.51(4) for phase IV].

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 structures: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); 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. 16550014) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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

References

Akhtaruzzaman, Md., Tomura, M. & Yamashita, Y. (2001). *Acta Cryst.* E**57**, *o*353–*o*355.

Andersen, E. K. (1967*a*). *Acta Cryst.* **22**, 188–191.

Andersen, E. K. (1967*b*). *Acta Cryst.* **22**, 191–196.

Anderson, E. K. (1967*c*). *Acta Cryst.* **22**, 196–201.

Asaji, T., Gotoh, K. & Watanabe, J. (2006). *J. Mol. Struct.* **791**, 89–92.

Benchekroun, R. & Savariault, J.-M. (1995). *Acta Cryst.* C**51**, 186–188.

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

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakreswki, V. G., Montgomery, J. A. Jr, Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G. A., Ayala, P. Y., Cui, Q., Morokuma, K., Malick, D. K., Rabuk, A. D., Raghavachari, K., Foresman, J. B., Cioslowki, J., Ortiz, J. V., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P. M. W., Johnson, B. G., Chen, W., Wong, M. W., Andres, J. L., Gonzalez, C., Head-Gordon, M., Replogle, E. S. & Pople, J. A. (1998). Gaussian 98, Revision A. **3**, Gaussian Inc., Pittsburgh, PA, USA.

Gotoh, K., Ishikawa, R. & Ishida, H. (2006). *Acta Cryst.* E**62**, *o*4738–*o*4740.

Hart, R. M., Whitehead, M. A. & Krause, L. (1972). *J. Chem. Phys.* **56**, 3038–3043.

Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.

Horiuchi, S., Ishii, F., Kumai, R., Okimoto, Y., Tachibana, H., Nagaosa, N. & Tokura, Y. (2005). *Nat. Mater.* **4**, 163–166.

Horiuchi, S. F., Kumai, R. & Tokura, Y. (2005). *J. Am. Chem. Soc.* **127**, 5010–5011.

Ikeda, R., Takahashi, S., Nihei, T., Ishihara, H. & Ishida, H. (2005). *Bull. Chem. Soc. Jpn*, **78**, 1241–1245.

Ishida, H. (2004*a*). *Acta Cryst.* E**60**, *o*1674–*o*1676.

Ishida, H. (2004*b*). *Acta Cryst.* E**60**, *o*1900–*o*1901.

Ishida, H. (2004*c*). *Acta Cryst.* E**60**, *o*2005–*o*2006.

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

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

Ishida, H. & Kashino, S. (1999*c*). *Acta Cryst.* C**55**, 1923–1926.

Ishida, H. & Kashino, S. (2002). *Z. Naturforsch. Teil A*, **57**, 829–836.

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

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

Rigaku/MSC (2004). *PROCESS-AUTO* and *CrystalStructure* (Version 3.7.0). Rigaku/MSC, New

Trails Drive, The Woodlands, TX, USA.

Saito, K., Amano, M., Yamamura, Y., Tojo, T. & Atake, T. (2006). *J. Phys. Soc. Jpn.* **75**, 033601–1–033601–3.

Seliger, J. (2006). private communication. University of Ljubljana, Slovenia.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

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

Tabuchi, Y., Takahashi, A., Gotoh, K., Akashi, H. & Ishida, H. (2005). *Acta Cryst.* E**61**, *o*4215–*o*4217.

Watanabe, J., Sekiguchi, M., Asaji, T., Gotoh, K. & Ishida, H. (2006). *Annual Meeting of Chem. Soc. Jpn. Tokyo, Japan*, 27–30 March, 2PC-021.

Zaman, Md. B., Tomura, M. & Yamashita, Y. (1999). *Chem. Commun.* 999–1000.

Zaman, Md. B., Tomura, M. & Yamashita, Y. (2000). *Org. Lett.* **2**, 273–275.

Zaman, Md. B., Udachin, K. A. & Ripmeester, J. A. (2004). *Cryst. Grwith Des.* **4**, 585–589.

Fig. 1. The molecular structure in phase II, showing the atom-numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.

Fig. 2. A packing diagram in phase II, viewed down the *b* axis. Dashed lines show O—H···N, O—H···O and C—H···O hydrogen bonds.

Fig. 3. The molecular structure in phase IV, showing the atom-numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.

Fig. 4. A packing diagram in phase IV, viewed down the *b* axis. Dashed lines show O—H···N, N—H···O, O—H···O and C—H···O hydrogen bonds.

Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

http://journals.iucr.org/c/journalhomepage.html

Table *S*1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for II*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl1	0.89399 (2)	0.33527 (8)	**0.425359** (16)	0.01844 (8)
Cl2	0.60368 (2)	0.94050 (8)	**0.076452** (16)	0.01829 (8)
O1	0.64260 (7)	0.3137 (4)	0.34692 (6)	0.0225 (2)
O2	0.97940 (7)	0.6859 (4)	0.30228 (5)	0.0206 (2)
O3	0.85625 (7)	0.9521 (4)	0.15579 (5)	0.0221 (2)
O4	0.51712 (7)	0.5933 (4)	0.20040 (6)	0.0218 (2)
N1	0.14612 (8)	0.0149 (4)	0.25139 (6)	0.0144 (2)
N2	0.35570 (8)	0.2719 (4)	0.24469 (6)	0.0147 (2)
C1	0.69369 (9)	0.4626 (5)	0.30487 (7)	0.0142 (2)
C2	0.81639 (9)	0.4974 (5)	0.33001 (7)	0.0141 (2)
C3	0.86824 (9)	0.6568 (5)	0.27988 (7)	0.0146 (2)
C4	0.80213 (9)	0.8079 (5)	0.19652 (7)	0.0152 (2)
C5	0.68088 (9)	0.7756 (5)	0.17171 (7)	0.0142 (2)
C6	0.62595 (9)	0.6178 (5)	0.22133 (7)	0.0148 (2)
C7	0.19125 (10)	0.2029 (5)	0.39323 (7)	0.0172 (3)
H7	0.1212	0.1145	0.3965	0.021
C8	0.26523 (10)	0.3594 (5)	0.46046 (7)	0.0189 (3)
H8	0.2465	0.3778	0.5107	0.023
C9	0.37031 (10)	0.4962 (5)	0.45659 (7)	0.0182 (3)
H9	0.4199	0.6082	0.5040	0.022
C10	0.40116 (9)	0.4694 (5)	0.38579 (7)	0.0169 (2)
H10	0.4717	0.5600	0.3841	0.020
C11	0.32631 (9)	0.3041 (5)	0.31480 (7)	0.0133 (2)
C12	0.21932 (9)	0.1721 (4)	0.31789 (7)	0.0137 (2)
C13	0.31169 (10)	0.0827 (5)	0.10280 (7)	0.0172 (3)
H13	0.3822	0.1673	0.0996	0.021
C14	0.23669 (10)	−0.0738 (5)	0.03530 (7)	0.0181 (3)
H14	0.2553	−0.0944	−0.0150	0.022
C15	0.13125 (10)	−0.2062 (5)	0.03932 (8)	0.0190 (3)
H15	0.0807	−0.3141	−0.0083	0.023
C16	0.10135 (10)	−0.1809 (5)	0.11044 (7)	0.0169 (2)
H16	0.0312	−0.2734	0.1124	0.020
C17	0.17663 (9)	−0.0138 (5)	0.18199 (7)	0.0138 (2)
C18	0.28334 (9)	0.1177 (5)	0.17761 (7)	0.0141 (2)
H2	1.0004 (18)	0.777 (8)	0.2720 (13)	0.047 (6)
H4	0.469 (3)	0.452 (15)	0.229 (2)	0.131 (14)

Table *S*2. *Anisotropic displacement parameters* ($Å^2$) *for II*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl1	0.01591 (11)	0.0239 (2)	0.01465 (11)	0.00002 (13)	0.00339 (9)	0.00369 (12)
Cl2	0.01625 (11)	0.0231 (2)	0.01447 (10)	0.00012 (13)	0.00313 (9)	0.00330 (12)
O1	0.0157 (3)	0.0322 (7)	0.0218 (4)	−0.0035 (5)	0.0092 (3)	0.0056 (5)
O2	0.0115 (3)	0.0303 (7)	0.0199 (4)	−0.0042 (5)	0.0047 (3)	0.0054 (5)
O3	0.0156 (3)	0.0322 (7)	0.0205 (4)	−0.0023 (5)	0.0083 (3)	0.0074 (5)
O4	0.0102 (3)	0.0318 (7)	0.0229 (4)	−0.0026 (5)	0.0043 (3)	0.0057 (5)
N1	0.0111 (3)	0.0161 (6)	0.0157 (4)	−0.0017 (4)	0.0038 (3)	0.0002 (4)
N2	0.0108 (3)	0.0175 (6)	0.0158 (4)	0.0000 (4)	0.0042 (3)	0.0019 (4)
C1	0.0116 (4)	0.0168 (6)	0.0151 (4)	−0.0011 (5)	0.0054 (3)	−0.0007 (5)
C2	0.0113 (4)	0.0177 (7)	0.0132 (4)	−0.0012 (5)	0.0037 (3)	0.0009 (5)
C3	0.0110 (4)	0.0180 (7)	0.0150 (4)	−0.0014 (5)	0.0041 (3)	−0.0006 (5)
C4	0.0144 (4)	0.0180 (7)	0.0138 (4)	−0.0019 (5)	0.0050 (3)	0.0007 (5)
C5	0.0117 (4)	0.0175 (7)	0.0132 (4)	−0.0010 (5)	0.0032 (3)	0.0012 (5)
C6	0.0131 (4)	0.0169 (7)	0.0143 (4)	−0.0015 (5)	0.0040 (3)	0.0005 (5)
C7	0.0138 (4)	0.0213 (7)	0.0175 (4)	0.0005 (5)	0.0063 (4)	0.0000 (5)

C8	0.0181 (4)	0.0223 (8)	0.0167 (4)	0.0015 (6)	0.0062 (4)	−0.0023 (5)
C9	0.0163 (4)	0.0196 (8)	0.0170 (4)	−0.0015 (5)	0.0026 (4)	−0.0046 (5)
C10	0.0123 (4)	0.0198 (7)	0.0170 (4)	0.0005 (5)	0.0020 (3)	−0.0006 (5)
C11	0.0105 (4)	0.0142 (6)	0.0154 (4)	0.0003 (5)	0.0041 (3)	0.0013 (4)
C12	0.0116 (4)	0.0148 (6)	0.0147 (4)	−0.0003 (4)	0.0040 (3)	0.0014 (4)
C13	0.0139 (4)	0.0211 (7)	0.0176 (4)	0.0001 (5)	0.0062 (4)	−0.0007 (5)
C14	0.0167 (4)	0.0211 (7)	0.0172 (4)	0.0018 (6)	0.0061 (4)	−0.0013 (5)
C15	0.0163 (5)	0.0217 (8)	0.0178 (4)	0.0017 (6)	0.0036 (4)	−0.0013 (5)
C16	0.0130 (4)	0.0189 (6)	0.0179 (4)	−0.0029 (5)	0.0032 (4)	−0.0023 (5)
C17	0.0110 (4)	0.0154 (7)	0.0145 (4)	−0.0002 (4)	0.0030 (3)	0.0012 (4)
C18	0.0100 (4)	0.0158 (6)	0.0165 (4)	0.0005 (4)	0.0041 (3)	0.0017 (4)

Table *S*3. *Geometric parameters (Å, °) for II*

Cl1—C2	1.7206 (12)	C7—C12	1.4258 (15)
Cl2—C5	1.7217 (12)	C7—H7	0.9500
O1—C1	1.2269 (15)	C8—C9	1.4254 (18)
O2—C3	1.3204 (13)	C8—H8	0.9500
O2—H2	0.73 (2)	C9—C10	1.3688 (17)
O3—C4	1.2291 (15)	C9—H9	0.9500
O4—C6	1.2923 (13)	C10—C11	1.4207 (19)
O4—H4	1.02 (4)	C10—H10	0.9500
N1—C12	1.3503 (17)	C11—C12	1.4367 (16)
N1—C17	1.3442 (14)	C13—C14	1.369 (2)
N2—C11	1.3493 (13)	C13—C18	1.4203 (15)
N2—C18	1.3472 (17)	C13—H13	0.9500
C1—C2	1.4583 (15)	C14—C15	1.4243 (18)
C1—C6	1.5251 (18)	C14—H14	0.9500
C2—C3	1.3547 (17)	C15—C16	1.3672 (16)
C3—C4	1.5115 (18)	C15—H15	0.9500
C4—C5	1.4404 (15)	C16—C17	1.4320 (19)
C5—C6	1.3713 (16)	C16—H16	0.9500
C7—C8	1.361 (2)	C17—C18	1.4399 (16)

C3—O2—H2	113.9 (17)	C10—C9—H9	119.4
C6—O4—H4	128 (2)	C8—C9—H9	119.4
C17—N1—C12	117.76 (10)	C9—C10—C11	119.13 (11)
C18—N2—C11	119.31 (10)	C9—C10—H10	120.4
O1—C1—C2	123.57 (11)	C11—C10—H10	120.4
O1—C1—C6	118.60 (10)	N2—C11—C10	120.00 (10)
C2—C1—C6	117.82 (10)	N2—C11—C12	120.19 (12)
C3—C2—C1	120.87 (11)	C10—C11—C12	119.80 (9)
C3—C2—Cl1	120.62 (9)	N1—C12—C7	119.65 (10)
C1—C2—Cl1	118.51 (9)	N1—C12—C11	121.24 (10)
O2—C3—C2	120.92 (11)	C7—C12—C11	119.10 (11)
O2—C3—C4	117.28 (10)	C14—C13—C18	119.54 (11)
C2—C3—C4	121.80 (10)	C14—C13—H13	120.2
O3—C4—C5	125.27 (11)	C18—C13—H13	120.2
O3—C4—C3	117.25 (10)	C13—C14—C15	120.97 (10)
C5—C4—C3	117.47 (10)	C13—C14—H14	119.5
C6—C5—C4	122.07 (11)	C15—C14—H14	119.5
C6—C5—Cl2	119.53 (9)	C16—C15—C14	121.26 (13)
C4—C5—Cl2	118.40 (9)	C16—C15—H15	119.4
O4—C6—C5	122.60 (11)	C14—C15—H15	119.4
O4—C6—C1	117.44 (10)	C15—C16—C17	119.50 (11)
C5—C6—C1	119.95 (10)	C15—C16—H16	120.3
C8—C7—C12	119.71 (11)	C17—C16—H16	120.3
C8—C7—H7	120.1	N1—C17—C16	119.26 (10)
C12—C7—H7	120.1	N1—C17—C18	121.81 (12)
C7—C8—C9	120.98 (10)	C16—C17—C18	118.93 (10)
C7—C8—H8	119.5	N2—C18—C13	120.53 (10)
C9—C8—H8	119.5	N2—C18—C17	119.68 (10)
C10—C9—C8	121.26 (12)	C13—C18—C17	119.79 (12)

O1—C1—C2—C3	178.25 (18)	C18—N2—C11—C10	−179.33 (17)
C6—C1—C2—C3	−1.2 (2)	C18—N2—C11—C12	0.6 (2)
O1—C1—C2—Cl1	−2.4 (2)	C9—C10—C11—N2	−179.34 (17)
C6—C1—C2—Cl1	178.15 (12)	C9—C10—C11—C12	0.8 (3)
C1—C2—C3—O2	−179.44 (14)	C17—N1—C12—C7	−178.95 (16)
Cl1—C2—C3—O2	1.2 (2)	C17—N1—C12—C11	−0.1 (2)
C1—C2—C3—C4	0.5 (2)	C8—C7—C12—N1	179.63 (18)
Cl1—C2—C3—C4	−178.81 (12)	C8—C7—C12—C11	0.7 (3)
O2—C3—C4—O3	−1.0 (2)	N2—C11—C12—N1	−0.2 (2)
C2—C3—C4—O3	178.99 (15)	C10—C11—C12—N1	179.74 (15)
O2—C3—C4—C5	179.78 (15)	N2—C11—C12—C7	178.73 (15)
C2—C3—C4—C5	−0.2 (2)	C10—C11—C12—C7	−1.4 (3)
O3—C4—C5—C6	−178.47 (18)	C18—C13—C14—C15	−0.8 (3)
C3—C4—C5—C6	0.7 (2)	C13—C14—C15—C16	0.1 (3)
O3—C4—C5—Cl2	1.7 (2)	C14—C15—C16—C17	0.9 (3)
C3—C4—C5—Cl2	−179.19 (12)	C12—N1—C17—C16	179.63 (17)
C4—C5—C6—O4	178.64 (16)	C12—N1—C17—C18	−0.1 (2)
Cl2—C5—C6—O4	−1.5 (2)	C15—C16—C17—N1	179.05 (17)
C4—C5—C6—C1	−1.4 (2)	C15—C16—C17—C18	−1.2 (3)
Cl2—C5—C6—C1	178.46 (12)	C11—N2—C18—C13	179.53 (17)
O1—C1—C6—O4	2.1 (2)	C11—N2—C18—C17	−0.7 (2)
C2—C1—C6—O4	−178.38 (15)	C14—C13—C18—N2	−179.78 (18)
O1—C1—C6—C5	−177.86 (15)	C14—C13—C18—C17	0.5 (3)
C2—C1—C6—C5	1.6 (2)	N1—C17—C18—N2	0.5 (2)
C12—C7—C8—C9	0.5 (3)	C16—C17—C18—N2	−179.22 (15)
C7—C8—C9—C10	−1.2 (3)	N1—C17—C18—C13	−179.74 (15)
C8—C9—C10—C11	0.5 (3)	C16—C17—C18—C13	0.5 (3)

Table *S*4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (*Å*^{2}) *for IV*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl1	0.89443 (2)	0.34823 (7)	**0.425784** (14)	0.01257 (7)
Cl2	0.60314 (2)	0.95781 (7)	**0.076336** (14)	0.01264 (7)
O1	0.64293 (7)	0.3279 (4)	0.34799 (5)	0.0159 (2)
O2	0.97889 (7)	0.7006 (4)	0.30178 (5)	0.0149 (2)
O3	0.85612 (7)	0.9680 (4)	0.15527 (5)	0.0152 (2)
O4	0.51724 (7)	0.6089 (4)	0.20120 (5)	0.0154 (2)
N1	0.14596 (8)	0.0307 (4)	0.25082 (5)	0.0104 (2)
N2	0.35549 (8)	0.2866 (4)	0.24450 (6)	0.0107 (2)
C1	0.69364 (9)	0.4768 (5)	0.30551 (6)	0.0106 (2)
C2	0.81630 (9)	0.5108 (4)	0.33036 (6)	0.0106 (2)
C3	0.86796 (9)	0.6705 (4)	0.27977 (6)	0.0107 (2)
C4	0.80181 (9)	0.8235 (4)	0.19621 (6)	0.0108 (2)
C5	0.68074 (9)	0.7914 (4)	0.17169 (6)	0.0100 (2)
C6	0.62582 (9)	0.6324 (4)	0.22164 (6)	0.0109 (2)
C7	0.19093 (9)	0.2174 (5)	0.39307 (7)	0.0123 (2)
H7	0.1207	0.1292	0.3961	0.015
C8	0.26493 (10)	0.3741 (5)	0.46075 (7)	0.0135 (2)
H8	0.2460	0.3927	0.5110	0.016
C9	0.37039 (10)	0.5106 (5)	0.45719 (7)	0.0128 (2)
H9	0.4200	0.6219	0.5049	0.015
C10	0.40151 (9)	0.4840 (5)	0.38619 (7)	0.0122 (2)
H10	0.4721	0.5749	0.3846	0.015
C11	0.32641 (9)	0.3182 (4)	0.31487 (6)	0.0094 (2)
C12	0.21931 (9)	0.1863 (4)	0.31773 (6)	0.0098 (2)
C13	0.31224 (9)	0.0996 (5)	0.10218 (7)	0.0122 (2)
H13	0.3828	0.1845	0.0992	0.015
C14	0.23704 (9)	−0.0559 (5)	0.03435 (7)	0.0127 (2)
H14	0.2555	−0.0756	−0.0161	0.015
C15	0.13155 (9)	−0.1886 (5)	0.03826 (7)	0.0132 (2)
H15	0.0811	−0.2965	−0.0096	0.016
C16	0.10142 (9)	−0.1639 (5)	0.10954 (7)	0.0120 (2)
H16	0.0310	−0.2558	0.1113	0.014
C17	0.17669 (9)	0.0011 (5)	0.18122 (6)	0.0103 (2)
C18	0.28358 (9)	0.1324 (4)	0.17703 (6)	0.0102 (2)
H2	1.0031 (18)	0.804 (7)	0.2700 (12)	0.043 (6)
H4	0.436 (2)	0.376 (10)	0.2351 (16)	0.091 (10)

Table *S*5. *Anisotropic displacement parameters* (Å^2) *for IV*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl1	0.01080 (11)	0.01619 (18)	0.01014 (9)	0.00005 (12)	0.00234 (8)	0.00243 (10)
Cl2	0.01160 (11)	0.01535 (18)	0.01017 (9)	0.00016 (12)	0.00214 (8)	0.00216 (10)
O1	0.0114 (3)	0.0224 (6)	0.0158 (3)	−0.0027 (5)	0.0068 (3)	0.0029 (4)
O2	0.0086 (3)	0.0218 (6)	0.0146 (3)	−0.0026 (4)	0.0041 (3)	0.0047 (4)
O3	0.0112 (3)	0.0212 (6)	0.0144 (3)	−0.0009 (5)	0.0059 (3)	0.0047 (4)
O4	0.0070 (3)	0.0219 (6)	0.0166 (3)	−0.0021 (4)	0.0027 (3)	0.0021 (4)
N1	0.0088 (3)	0.0111 (6)	0.0108 (3)	−0.0018 (4)	0.0024 (3)	−0.0004 (3)
N2	0.0077 (3)	0.0127 (6)	0.0119 (3)	0.0010 (4)	0.0035 (3)	0.0019 (4)
C1	0.0090 (4)	0.0122 (6)	0.0109 (4)	−0.0003 (5)	0.0035 (3)	−0.0003 (5)
C2	0.0085 (4)	0.0139 (7)	0.0094 (3)	−0.0009 (5)	0.0026 (3)	0.0009 (4)
C3	0.0084 (4)	0.0123 (6)	0.0111 (4)	−0.0008 (4)	0.0024 (3)	−0.0006 (4)
C4	0.0107 (4)	0.0118 (6)	0.0102 (4)	−0.0013 (5)	0.0035 (3)	−0.0005 (5)
C5	0.0083 (4)	0.0116 (6)	0.0096 (3)	−0.0005 (5)	0.0020 (3)	0.0008 (4)
C6	0.0102 (4)	0.0120 (6)	0.0103 (4)	−0.0007 (4)	0.0027 (3)	0.0004 (4)
C7	0.0100 (4)	0.0148 (6)	0.0129 (4)	0.0003 (5)	0.0045 (3)	0.0005 (4)
C8	0.0129 (4)	0.0153 (7)	0.0126 (4)	0.0000 (5)	0.0046 (3)	−0.0019 (4)
C9	0.0112 (4)	0.0136 (7)	0.0126 (4)	−0.0015 (5)	0.0019 (3)	−0.0031 (4)
C10	0.0091 (4)	0.0134 (6)	0.0129 (4)	0.0007 (5)	0.0016 (3)	−0.0005 (5)
C11	0.0076 (4)	0.0096 (6)	0.0110 (4)	−0.0001 (4)	0.0030 (3)	0.0005 (4)
C12	0.0084 (4)	0.0100 (6)	0.0110 (4)	0.0000 (4)	0.0031 (3)	0.0010 (4)
C13	0.0098 (4)	0.0141 (6)	0.0132 (4)	0.0001 (5)	0.0042 (3)	−0.0007 (4)
C14	0.0114 (4)	0.0145 (6)	0.0125 (4)	0.0021 (5)	0.0042 (3)	−0.0002 (4)
C15	0.0115 (4)	0.0149 (7)	0.0124 (4)	0.0020 (5)	0.0027 (3)	−0.0003 (5)

C16	0.0091 (4)	0.0134 (6)	0.0128 (4)	−0.0023 (5)	0.0021 (3)	−0.0013 (5)
C17	0.0084 (4)	0.0117 (7)	0.0105 (4)	0.0005 (4)	0.0024 (3)	0.0010 (4)
C18	0.0068 (4)	0.0111 (6)	0.0126 (4)	0.0000 (4)	0.0026 (3)	0.0010 (4)

Table *S*6. *Geometric parameters (Å, °) for IV*

Cl1—C2	1.7203 (12)	C7—C12	1.4249 (14)
Cl2—C5	1.7229 (12)	C7—H7	0.9500
O1—C1	1.2259 (15)	C8—C9	1.4267 (17)
O2—C3	1.3191 (13)	C8—H8	0.9500
O2—H2	0.79 (2)	C9—C10	1.3710 (16)
O3—C4	1.2310 (15)	C9—H9	0.9500
O4—C6	1.2901 (13)	C10—C11	1.4234 (18)
N1—C12	1.3502 (15)	C10—H10	0.9500
N1—C17	1.3467 (13)	C11—C12	1.4358 (15)
N2—C11	1.3487 (13)	C13—C14	1.3696 (18)
N2—C18	1.3466 (16)	C13—C18	1.4194 (14)
N2—H4	1.12 (3)	C13—H13	0.9500
C1—C2	1.4585 (15)	C14—C15	1.4239 (17)
C1—C6	1.5269 (17)	C14—H14	0.9500
C2—C3	1.3564 (16)	C15—C16	1.3686 (14)
C3—C4	1.5136 (17)	C15—H15	0.9500
C4—C5	1.4390 (15)	C16—C17	1.4269 (18)
C5—C6	1.3743 (16)	C16—H16	0.9500
C7—C8	1.3636 (18)	C17—C18	1.4399 (16)
C3—O2—H2	115.6 (15)	C10—C9—H9	119.4
C17—N1—C12	117.84 (10)	C8—C9—H9	119.4
C18—N2—C11	119.74 (10)	C9—C10—C11	118.98 (11)
C18—N2—H4	113.8 (14)	C9—C10—H10	120.5
C11—N2—H4	126.4 (14)	C11—C10—H10	120.5
O1—C1—C2	123.45 (11)	N2—C11—C10	120.07 (10)
O1—C1—C6	118.78 (10)	N2—C11—C12	119.99 (11)
C2—C1—C6	117.76 (10)	C10—C11—C12	119.94 (9)
C3—C2—C1	120.82 (10)	N1—C12—C7	119.64 (10)
C3—C2—Cl1	120.50 (8)	N1—C12—C11	121.25 (9)
C1—C2—Cl1	118.67 (8)	C7—C12—C11	119.11 (11)
O2—C3—C2	121.07 (11)	C14—C13—C18	119.28 (11)
O2—C3—C4	116.98 (10)	C14—C13—H13	120.4
C2—C3—C4	121.95 (10)	C18—C13—H13	120.4
O3—C4—C5	125.49 (11)	C13—C14—C15	120.99 (10)
O3—C4—C3	117.19 (10)	C13—C14—H14	119.5
C5—C4—C3	117.32 (10)	C15—C14—H14	119.5
C6—C5—C4	122.15 (10)	C16—C15—C14	121.34 (12)
C6—C5—Cl2	119.41 (8)	C16—C15—H15	119.3
C4—C5—Cl2	118.44 (8)	C14—C15—H15	119.3
O4—C6—C5	122.75 (11)	C15—C16—C17	119.41 (11)
O4—C6—C1	117.27 (10)	C15—C16—H16	120.3
C5—C6—C1	119.98 (10)	C17—C16—H16	120.3
C8—C7—C12	119.75 (11)	N1—C17—C16	119.27 (10)
C8—C7—H7	120.1	N1—C17—C18	121.76 (11)
C12—C7—H7	120.1	C16—C17—C18	118.96 (9)
C7—C8—C9	120.96 (10)	N2—C18—C13	120.58 (10)
C7—C8—H8	119.5	N2—C18—C17	119.41 (9)
C9—C8—H8	119.5	C13—C18—C17	120.01 (11)
C10—C9—C8	121.25 (11)		

O1—C1—C2—C3	178.28 (17)	C18—N2—C11—C10	−179.39 (16)
C6—C1—C2—C3	−1.0 (2)	C18—N2—C11—C12	0.3 (2)
O1—C1—C2—Cl1	−2.4 (2)	C9—C10—C11—N2	−179.52 (16)
C6—C1—C2—Cl1	178.29 (12)	C9—C10—C11—C12	0.8 (2)
C1—C2—C3—O2	−179.71 (14)	C17—N1—C12—C7	−178.92 (15)
Cl1—C2—C3—O2	1.0 (2)	C17—N1—C12—C11	0.4 (2)
C1—C2—C3—C4	0.6 (2)	C8—C7—C12—N1	179.93 (17)
Cl1—C2—C3—C4	−178.68 (12)	C8—C7—C12—C11	0.6 (2)
O2—C3—C4—O3	−0.7 (2)	N2—C11—C12—N1	−0.2 (2)
C2—C3—C4—O3	178.94 (15)	C10—C11—C12—N1	179.41 (15)
O2—C3—C4—C5	179.92 (14)	N2—C11—C12—C7	179.05 (14)
C2—C3—C4—C5	−0.4 (2)	C10—C11—C12—C7	−1.3 (2)
O3—C4—C5—C6	−178.63 (17)	C18—C13—C14—C15	−0.8 (3)
C3—C4—C5—C6	0.7 (2)	C13—C14—C15—C16	0.3 (3)
O3—C4—C5—Cl2	1.5 (2)	C14—C15—C16—C17	0.6 (2)
C3—C4—C5—Cl2	−179.17 (11)	C12—N1—C17—C16	179.62 (16)
C4—C5—C6—O4	178.41 (15)	C12—N1—C17—C18	−0.5 (2)
Cl2—C5—C6—O4	−1.8 (2)	C15—C16—C17—N1	178.84 (16)
C4—C5—C6—C1	−1.1 (2)	C15—C16—C17—C18	−1.0 (2)
Cl2—C5—C6—C1	178.73 (11)	C11—N2—C18—C13	179.45 (15)
O1—C1—C6—O4	2.4 (2)	C11—N2—C18—C17	−0.4 (2)
C2—C1—C6—O4	−178.27 (14)	C14—C13—C18—N2	−179.48 (17)
O1—C1—C6—C5	−178.08 (15)	C14—C13—C18—C17	0.4 (2)
C2—C1—C6—C5	1.3 (2)	N1—C17—C18—N2	0.5 (2)
C12—C7—C8—C9	0.5 (3)	C16—C17—C18—N2	−179.59 (15)
C7—C8—C9—C10	−1.0 (3)	N1—C17—C18—C13	−179.31 (15)
C8—C9—C10—C11	0.3 (2)	C16—C17—C18—C13	0.6 (2)