

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*}

^aDepartment of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan, and ^bDepartment of Chemistry, Graduate School of Integrated Basic Sciences, College of Humanities and Sciences, Nihon University, Tokyo 156-8550, Japan

Correspondence e-mail: ishidah@cc.okayama-u.ac.jp

Received 20 September 2006

Accepted 18 November 2006

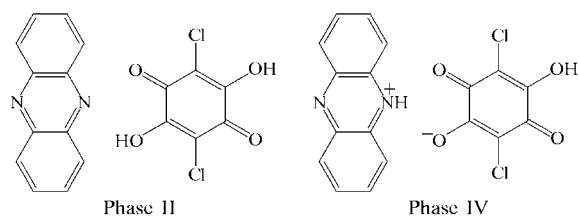
Online 12 December 2006

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 [phenazine–chloranilic acid (1/1), C₁₂H₈N₂·C₆H₂Cl₂O₄, in phase II, and phenazinium hydrogen chloranilate, C₁₂H₉N₂⁺·C₆HCl₂O₄⁻, in phase IV], have been determined. Both phases crystallize in *P*₂₁, and each 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 the chloranilic acid molecule 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) and 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 phenazine and chloranilic acid 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 *P*₂₁, while the space group is *P*₂₁/*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 phenazine–deuterated chloranilic acid (1/1), C₁₂H₈N₂·C₆D₂Cl₂O₄, indicating the significant effect of the hydrogen bonding on the phase tran-

sition. In these phases, we have measured the temperature dependence of ³⁵Cl 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 *P*₂₁/*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 molecule has lost its centre of symmetry and that the two Cl atoms in the chloranilic acid molecule are inequivalent in phase II. This observation excludes the centrosymmetric space group *P*₂₁/*n* in phase II and is consistent with the space group *P*₂₁ 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 ¹⁴N NQR measurements (Seliger, 2006). Furthermore, the existence of a hydrogen-transfer motion in the hydrogen bond was suggested from the ³⁵Cl 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 reappear can be assigned to the transition points corresponding to those observed by heat capacity

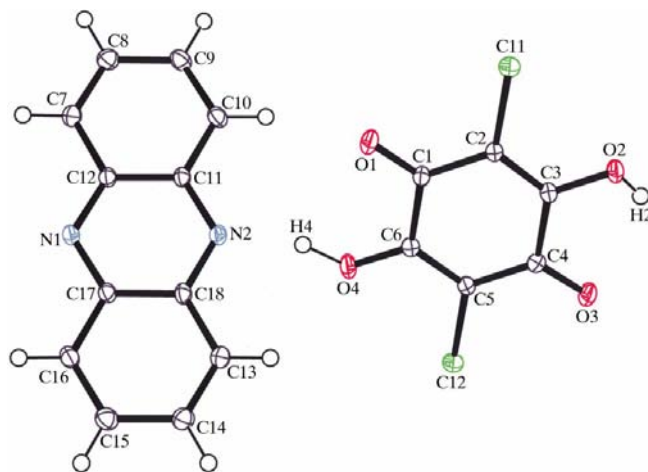


Figure 1
The molecular structure in phase II, showing the atom-numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.

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 molecule changes from neutral in phase II to a monovalent 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 redetermined 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) and 1.5251 (18) Å], which is explainable in terms of the double π system of the anion (Andersen, 1967c; Benchekroun & Savariault, 1995). In the crystal structure, 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 with respect to each other, 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 atom H4, which is involved in the shorter O—H...N hydrogen bond (O4—H4...N2), has a considerably larger U_{iso} value [0.131 (14) Å²] than the H atom [H2; 0.047 (6) Å²] involved in the longer O—H...N hydrogen bond (O2—H2...N1¹; 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 atom H4

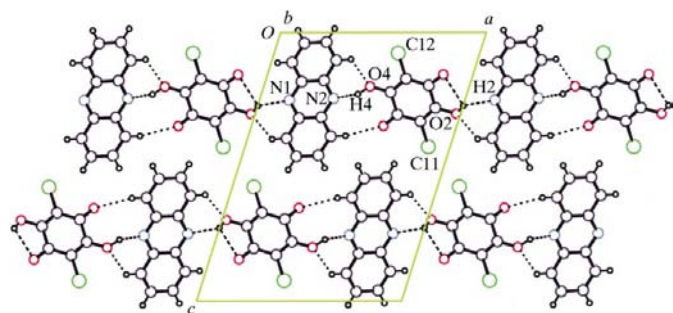


Figure 2
The packing in phase II, viewed down the *b* axis. Dashed lines indicate O—H...N, O—H...O and C—H...O hydrogen bonds.

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 the 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, 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...O4 and O2—H2...N1¹ hydrogen bonds (symmetry code as in Table 4), forming a chain running along the [110] direction (Fig. 4). The O4...N2 distance is shorter than that in phase II, while the O2...N1 distance is longer. 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. The $U_{\text{iso}}(\text{H})$ value of H4 is still rather large [0.091 (10) Å²] and the N2—H4 bond is long, suggesting that atom H4 is also disordered in this phase.

Typical C=O and C—O(–H) bond lengths in neutral chloranilic acid are 1.22 (1) and 1.32 (1) Å, respectively (Andersen, 1967a,b; Zaman *et al.*, 2004), and those of C=O and C—O[–] in the chloranilate monoanion are 1.24 (2) and 1.25 (2) Å. The values are somewhat scattered and depend on the hydrogen-bonding scheme around the O atoms (Ishida & Kashino, 1999a, 2002; Ishida, 2004a; 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 and

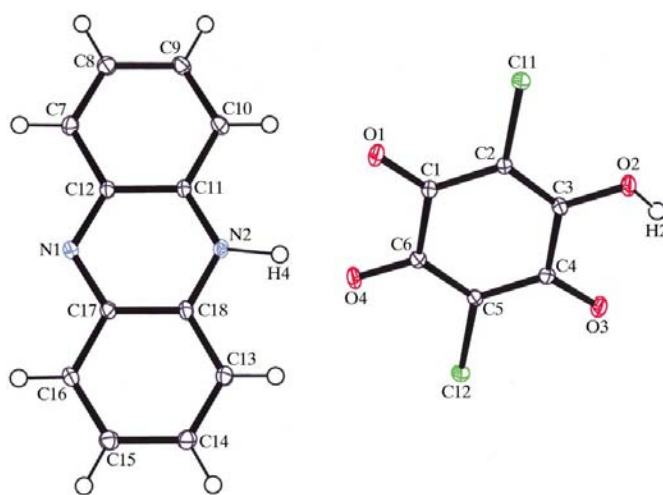


Figure 3
The molecular structure in phase IV, showing the atom-numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.

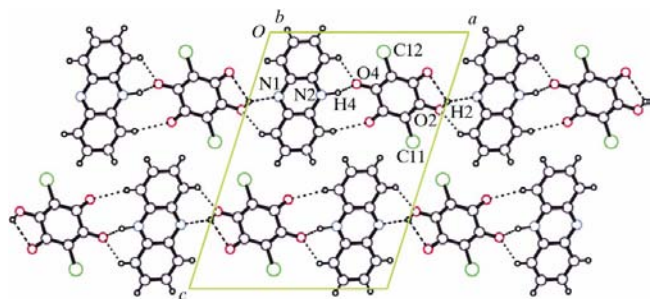


Figure 4
The packing in phase IV, viewed down the *b* axis. Dashed lines indicate O—H...N, N—H...O, O—H...O and C—H...O hydrogen bonds.

C3—O2(—H2); Table 1], but those in the other system [C4=O3 and C6—O4(—H4)] deviate slightly from the above values. Taking account of both this and the NQR results, we conclude that the chloranilic acid molecule in phase II has a charge close to, but not exactly, zero as a result of 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 1.3191 (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 bonds 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 -1 , as a result of the proton motion in the hydrogen bond. The difference in C—N bond lengths between phase II and IV is also small, again probably because of the proton motion, although a detectable difference can be expected from the calculated bond lengths for the isolated phenazine molecule and the phenazinium cation in the gas phase at the B3LYP/6-311G(2*d*,2*p*) level of theory by using the GAUSSIAN98 program (Frisch *et al.*, 1998); the calculated C—N bond length in phenazine is 1.3373 Å, while the C—N⁺(—H) and C—N lengths in 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.

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).

Phase II

Crystal data

C₁₂H₈N₂·C₆H₂Cl₂O₄
M_r = 389.19
 Monoclinic, $P2_1$
a = 12.4268 (2) Å
b = 3.7960 (1) Å
c = 16.9218 (3) Å
 β = 107.812 (1)°
V = 759.97 (3) Å³

Z = 2
D_x = 1.701 Mg m^{−3}
 Mo *K*α radiation
 μ = 0.46 mm^{−1}
T = 170 (2) K
 Block, brown
 0.40 × 0.25 × 0.25 mm

Data collection

Rigaku R-Axis 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_{int} = 0.052
 θ_{\max} = 40.2°

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.034
 $wR(F^2)$ = 0.097
S = 1.06
 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
 $\Delta\rho_{\max}$ = 0.56 e Å^{−3}
 $\Delta\rho_{\min}$ = −0.38 e Å^{−3}
 Absolute structure: Flack (1983),
 3778 Friedel pairs
 Flack parameter: 0.48 (5)

Table 1

Selected bond lengths (Å) for phase II.

| | | | |
|--------|-------------|--------|-------------|
| C1—C2 | 1.7206 (12) | O4—C6 | 1.2923 (13) |
| C12—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-bond geometry (Å, °) for phase II.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| O2—H2...O3 | 0.73 (2) | 2.32 (2) | 2.6809 (13) | 113 (2) |
| O2—H2...N1 ⁱ | 0.73 (2) | 2.15 (2) | 2.7722 (16) | 145 (2) |
| O4—H4...N2 | 1.02 (4) | 1.66 (4) | 2.6446 (16) | 159 (3) |
| C7—H7...O2 ⁱⁱ | 0.95 | 2.56 | 3.2668 (19) | 131 |
| C10—H10...O1 | 0.95 | 2.57 | 3.3153 (15) | 136 |
| C13—H13...O4 | 0.95 | 2.57 | 3.2283 (19) | 127 |

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

Phase IV

Crystal data

C₁₂H₉N₂⁺·C₆HCl₂O₄[−]
M_r = 389.19
 Monoclinic, $P2_1$
a = 12.4320 (3) Å
b = 3.7702 (1) Å
c = 16.8848 (4) Å
 β = 107.778 (1)°
V = 753.62 (3) Å³

Z = 2
D_x = 1.715 Mg m^{−3}
 Mo *K*α radiation
 μ = 0.46 mm^{−1}
T = 93 (2) K
 Block, brown
 0.40 × 0.25 × 0.25 mm

Data collection

Rigaku R-Axis 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_{int} = 0.037
 θ_{\max} = 40.3°

Refinement

| | |
|--|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.1204P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.089$ | $(\Delta/\sigma)_{\max} = 0.001$ |
| $S = 1.06$ | $\Delta\rho_{\max} = 0.54 \text{ e } \text{\AA}^{-3}$ |
| 8923 reflections | $\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$ |
| 245 parameters | Absolute structure: Flack (1983), |
| H atoms treated by a mixture of independent and constrained refinement | 3684 Friedel pairs |
| | Flack parameter: 0.51 (4) |

Table 3
Selected bond lengths (Å) for phase 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-bond geometry (Å, °) for phase 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) $x + 1, y + 1, z$; (ii) $x - 1, y - 1, z$.

For both phases, H atoms attached to O and N atoms were found in a difference Fourier map and refined isotropically. Refined distances are given in Tables 2 and 4. Other H atoms were treated as riding, with $C-H = 0.95 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. The present refinement gives a slightly better result than the refinement with distance restraints [$O-H = 0.82 (1) \text{ \AA}$ or $N-H = 0.87 (1) \text{ \AA}$] in terms of the residual electron densities around N and O atoms. Crystals in phases 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 pseudosymmetry ($P2_1/n$), 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 phases 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 phases II and IV. The Flack parameters for phases II and IV before the final refinement were 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 phases, data collection: PROCESS-AUTO (Rigaku/MS, 2004); cell refinement: PROCESS-AUTO; data reduction: Crystal-

Structure (Rigaku/MS, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (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: BM3017). Services for accessing these data are described at the back of the journal.

References

Akhtaruzzaman, M., Tomura, M. & Yamashita, Y. (2001). *Acta Cryst.* **E57**, o353–o355.

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

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

Andersen, E. K. (1967c). *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.* **C51**, 186–188.

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

Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.

Frisch, M. J. *et al.* (1998). GAUSSIAN98. Revision A.3. Gaussian Inc., Pittsburgh, PA, USA.

Gotoh, K., Ishikawa, R. & Ishida, H. (2006). *Acta Cryst.* **E62**, o4738–o4740.

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. (2004a). *Acta Cryst.* **E60**, o1674–o1676.

Ishida, H. (2004b). *Acta Cryst.* **E60**, o1900–o1901.

Ishida, H. (2004c). *Acta Cryst.* **E60**, o2005–o2006.

Ishida, H. & Kashino, S. (1999a). *Acta Cryst.* **C55**, 1149–1152.

Ishida, H. & Kashino, S. (1999b). *Acta Cryst.* **C55**, 1714–1717.

Ishida, H. & Kashino, S. (1999c). *Acta Cryst.* **C55**, 1923–1926.

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

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

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

Rigaku/MS (2004). PROCESS-AUTO and CrystalStructure (Version 3.7.0). Rigaku/MS, The Woodlands, Texas, 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.* **E61**, o4215–o4217.

Watanabe, J., Sekiguchi, M., Asaji, T., Gotoh, K. & Ishida, H. (2006). Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, 27–30 March, 2PC–021.

Zaman, Md. B., Tomura, M. & Yamashita, Y. (1999). *Chem. Commun.* pp. 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. Growth Des.* **4**, 585–589.