Acta Cryst. (1997). C**53**, 602-605

α and β Phases of 4-Aminoquinoline-2-carboxylic Acid Monohydrate

Craig J. Burd, Allison J. Dobson and Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

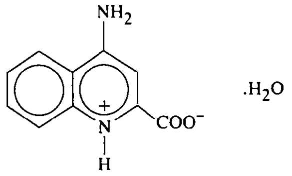
(*Received 14 October 1996; accepted 14 January 1997*)

Abstract

The structures of two phases of the title compound, $C_{10}H_8N_2O_2.H_2O$, are reported. While the organic molecule has very nearly the same molecular geometry in the two phases, the hydrogen-bonding patterns are quite different. In each case, however, a three-dimensional network of hydrogen bonds is formed. In the α phase, six N—H···O hydrogen bonds have donor–acceptor distances ranging from 2.681 (2) to 3.206 (2) Å, while three O—H···O hydrogen bonds range from 2.837 (2) to 3.173 (2) Å, and in the β phase, four N—H···O hydrogen bonds range from 2.668 (2) to 3.038 (2) Å, while two O—H···O hydrogen bonds are 2.951 (3) and 2.959 (3) Å in length.

Comment

This study of 4-aminoquinoline-2-carboxylic acid monohydrate, (I), is one of a series of studies of hydrogen bonding in carboxylic acids and follows a study of the somewhat similar 2-phenylquinoline-4-carboxylic acid (Blackburn, Dobson & Gerkin, 1996).



(I)

In the title phases, the quinoline core geometries are very nearly indistinguishable. For the 11 core bonds, the r.m.s. difference of corresponding lengths is 0.003 Å, the e.s.d.'s for the α and β distances being 0.002 and 0.003 Å, respectively. For the core angles, the r.m.s. difference for 14 corresponding pairs is 0.4°, the e.s.d.'s for the α and β angles being 0.1 and 0.2°, respectively. Furthermore, the cores are quite similar in their degree of planarity, though the α core is slightly flatter; for α, the maximum deviation of a core atom from the best-fit core plane is 0.020 (1) Å and the average deviation 0.009 (1) Å, while for β, the corresponding values are 0.032 (2) and 0.019 (2) Å.

In the α phase, the dihedral angles made by the carboxyl and amino group planes with the core plane are 6.60 (6) and 11.3 (15)°, respectively, and the angle they make with one another is 17.5 (15)°. The corresponding values for the β phase are 9.62 (10), 6.9 (14) and 15.9 (16)°. Moreover, in each phase, the carboxyl H atom has been transferred to the ring N atom. The entire organic molecular configurations in the two phases are thus quite similar.

The molecular arrangement and the hydrogen bonding of the two phases are depicted in Fig. 2. In each case, all of the hydrogen bonds of a central organic molecule and the water molecule associated with it are shown. Also in each case, a three-dimensional network of hydrogen bonds is developed, but the α phase is more richly bonded. In particular, only in the α phase do the amino group H atoms have the water oxygen as an acceptor in addition to carboxyl O1 and O2 atoms. The parameters for the hydrogen bonds for both phases are given in Table 3.

In the α phase, all the quinoline core planes are parallel. In the β phase, the dihedral angle between the core planes of the two non-parallel sets of molecules is 43.51 (4)°.

For comparison with a different yet similar molecule, 2-phenylquinoline-4-carboxylic acid (Blackburn, Dobson & Gerkin, 1996) was chosen. The r.m.s. differences of the means of corresponding α and β core distances and the 11 corresponding core distances in 2-phenylquinoline-4-carboxylic acid were obtained; for the six bonds in the carbocyclic rings, the r.m.s. deviation is 0.010 Å and for the six bonds in the heterocyclic rings (which are the rings carrying diverse substituents), the r.m.s. deviation is 0.029 Å. Further useful comparison is afforded by 4,8-dihydroxyquinoline-2-carboxylic acid monohydrate (xanthurenic acid monohydrate, hereafter XAM; Okabe, Miura & Shimosaki, 1996). The r.m.s. differences of the means of corresponding α and β core distances and the 11 corresponding core distances in XAM we calculate to be 0.006 Å for the six bonds of the carbocyclic ring and 0.009 Å for the six bonds of the heterocyclic ring; since the e.s.d. of the individual distances is 0.003 Å for the title compound and 0.005 Å for XAM, the agreement of the core distances is very good. The degrees of planarity of the quinoline cores of the β phase of both the title compound and XAM are also very similar; the maximum deviations of the core atom from the best-fit core plane are 0.032 (2) and 0.030 Å (our calculation). In the title compound, the dihedral angles between the core plane and the carboxyl group plane are small (~6.6 and ~9.6° for the α and β phases, respectively); in XAM, this angle is ~4.9° (our calculation), a quite comparable value (Okabe *et al.* state, apparently in only a qualitative sense, that the carboxyl group and the quinoline ring are coplanar). Finally, in

XAM, as in the title compound, H-atom transfer occurs from the carboxyl group to the ring N atom and a very similar intramolecular hydrogen bond is formed involving a carboxyl O atom, the ring N atom and the H atom on the ring N atom.

In the α phase, the closest intermolecular approaches, excluding pairs of atoms both of which are involved in hydrogen bonding, are between O1 and H5$^{\text{ix}}$ [symmetry code: (ix) x, $y-1$, z], and between C11 and H1O$^{\text{iv}}$

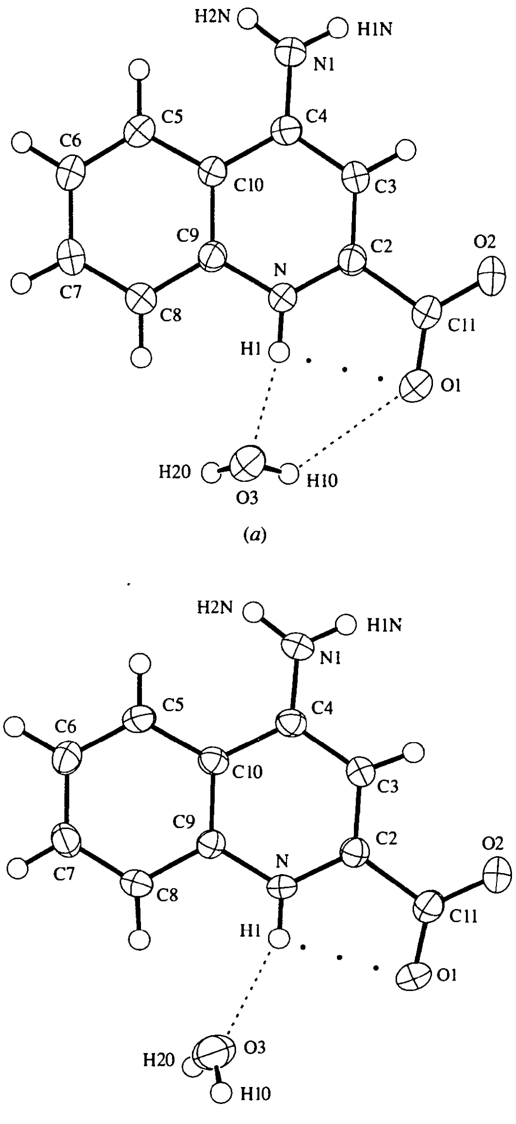


Fig. 1. *ORTEP*II (Johnson, 1976) drawings of 4-aminoquinoline-2-carboxylic acid monohydrate showing the atomic numbering schemes for (*a*) the α phase and (*b*) the β phase. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small. Intermolecular hydrogen bonds are indicated by dashed lines and intramolecular hydrogen bonds by dotted lines.

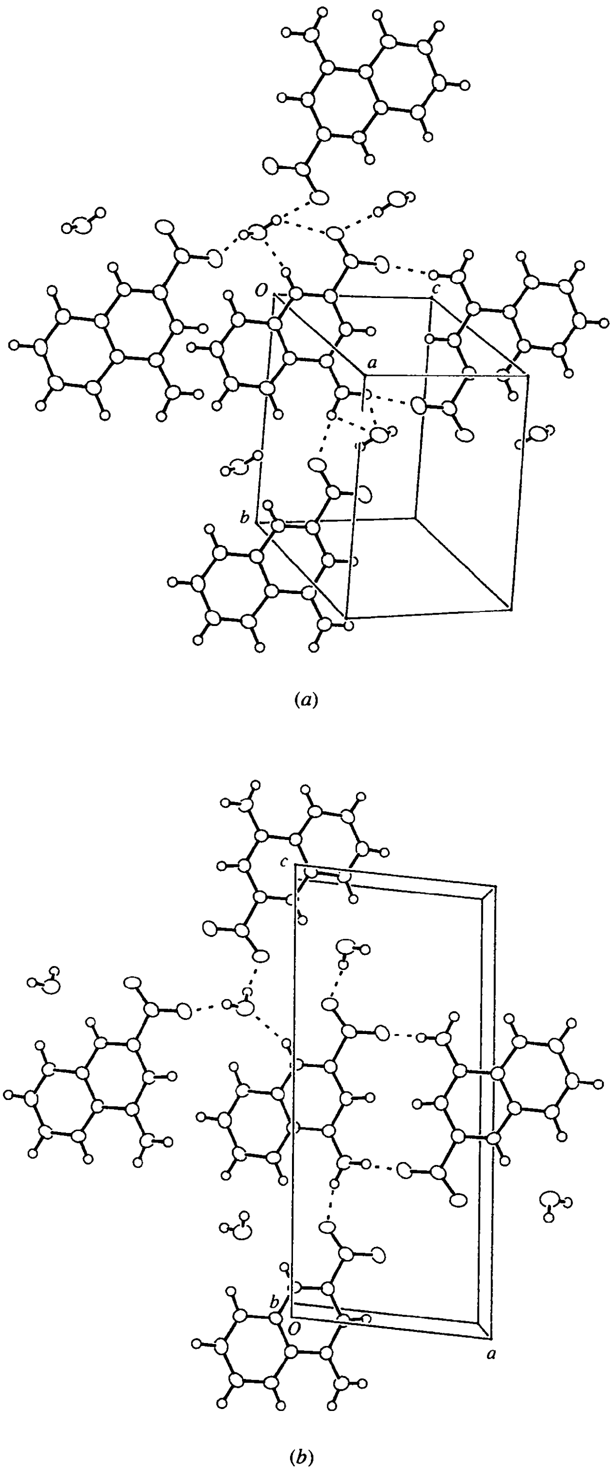


Fig. 2. *ORTEP*II (Johnson, 1976) diagrams of (*a*) the α phase and (*b*) the β phase of 4-aminoquinoline-2-carboxylic acid monohydrate, showing a central acid molecule and its associated water molecule, and all the molecules to which these are directly hydrogen bonded. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small. Hydrogen bonds (intermolecular) are indicated by dashed lines.

[symmetry code: (iv) $1-x$, $-1-y$, $-z$], which fall short of the corresponding Bondi (1964) radius sums by 0.31 and 0.26 Å, respectively. Although the H5 and C11 atoms are not involved in hydrogen bonding, the molecules in which O1 and $H5^{ix}$, and C11 and $H1O^{iv}$ occur are hydrogen bonded to one another. Three additional close approaches, all involving H atoms, also fall short of the corresponding Bondi sums by 0.10 Å or more. Similarly, for the β phase, the closest approaches are between O3 and $H8^{x}$ [symmetry code: (x) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$], and O1 and $H5^{x}$, which fall short of the Bondi radius sum by 0.42 and 0.25 Å, respectively. As above, although H8 and H5 are not involved in hydrogen bonding, the molecules in which atoms O1 and $H5^{x}$, and O3 and $H8^{x}$ occur are hydrogen bonded to one another. No other close approach in the β phase is appreciably less than the corresponding Bondi radius sum.

Experimental

4-Aminoquinoline-2-carboxylic acid was obtained from the Sigma–Aldrich Chemical Company. The two title phases were obtained as follows: for the α phase, the compound was dissolved in hot water and treated with Norit A decolorizing carbon. The mixture was filtered and the filtrate was allowed to cool. Evaporation at room temperature produced suitable crystals subsequently designated as the α phase. For the β phase, the compound was dissolved in an acetone–water solution with slight heating, the solution treated with Norit A and the resulting mixture filtered. The filtrate was allowed to evaporate very slowly at room temperature. This resulted in usable crystals of a second phase designated as the β phase.

Compound (I) – α phase

Crystal data

$C_{10}H_8N_2O_2.H_2O$
$M_r = 206.20$
Triclinic
$P\overline{1}$
$a = 7.602\,(1)$ Å
$b = 8.662\,(1)$ Å
$c = 7.505\,(1)$ Å
$\alpha = 94.64\,(1)°$
$\beta = 96.48\,(1)°$
$\gamma = 67.20\,(1)°$
$V = 452.3\,(1)$ Å^3
$Z = 2$
$D_x = 1.514$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.8$–$17.3°$
$\mu = 0.107$ mm^{-1}
$T = 296$ K
Cut plate
$0.38 \times 0.34 \times 0.34$ mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
2253 measured reflections
2094 independent reflections
1774 reflections with $I > \sigma(I)$

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -9 \rightarrow 9$
6 standard reflections every 150 reflections intensity decay: 3.5%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.055$
$S = 2.30$
1774 reflections
176 parameters
All H atoms refined
$w = 1/\sigma F^2$

$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: none
Scattering factors from Stewart, Davidson & Simpson (1965) and Cromer & Waber (1974)

Compound (I) – β phase

Crystal data

$C_{10}H_8N_2O_2.H_2O$
$M_r = 206.20$
Monoclinic
$P2_1/c$
$a = 7.378\,(1)$ Å
$b = 7.306\,(1)$ Å
$c = 16.833\,(1)$ Å
$\beta = 95.544\,(7)°$
$V = 903.0\,(2)$ Å^3
$Z = 4$
$D_x = 1.516$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.5$–$17.5°$
$\mu = 0.107$ mm^{-1}
$T = 296$ K
Prism
$0.35 \times 0.35 \times 0.12$ mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
2430 measured reflections
2263 independent reflections
1440 reflections with $I > \sigma(I)$

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = -21 \rightarrow 21$
6 standard reflections every 150 reflections intensity decay: 4.9%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.054$
$S = 1.67$
1440 reflections
177 parameters
All H atoms refined
$w = 1/\sigma F^2$
$(\Delta/\sigma)_{\rm max} < 0.01$

$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $1.7\,(5) \times 10^{-6}$
Scattering factors from Stewart, Davidson & Simpson (1965) and Cromer & Waber (1974)

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

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

	x	y	z	$U_{\rm eq}$
α phase				
O1	0.3479 (2)	−0.3814 (1)	0.1438 (1)	0.0473 (3)
O2	0.4004 (2)	−0.2709 (1)	0.4142 (1)	0.0460 (3)
O3	0.2704 (2)	−0.3499 (1)	−0.2787 (2)	0.0445 (3)
N	0.2535 (2)	−0.0876 (1)	−0.0097 (2)	0.0292 (3)
N1	0.3257 (2)	0.3131 (2)	0.2763 (2)	0.0377 (3)

C2	0.3148 (2)	−0.0993 (2)	0.1653 (2)	0.0276 (3)
C3	0.3371 (2)	0.0340 (2)	0.2624 (2)	0.0297 (3)
C4	0.2990 (2)	0.1857 (2)	0.1814 (2)	0.0285 (3)
C5	0.1843 (2)	0.3447 (2)	−0.1020 (2)	0.0334 (4)
C6	0.1175 (2)	0.3495 (2)	−0.2789 (2)	0.0361 (4)
C7	0.0937 (2)	0.2101 (2)	−0.3685 (2)	0.0348 (4)
C8	0.1393 (2)	0.0652 (2)	−0.2807 (2)	0.0334 (4)
C9	0.2073 (2)	0.0581 (2)	−0.0981 (2)	0.0272 (3)
C10	0.2293 (2)	0.1985 (2)	−0.0055 (2)	0.0267 (3)
C11	0.3579 (2)	−0.2664 (2)	0.2489 (2)	0.0319 (3)
β phase				
O1	0.1780 (2)	0.1420 (3)	0.70011 (9)	0.0412 (5)
O2	0.4441 (2)	0.0991 (3)	0.64898 (9)	0.0428 (5)
O3	−0.2536 (3)	0.3639 (3)	0.6732 (1)	0.0471 (6)
N	0.0144 (2)	0.2395 (3)	0.55814 (10)	0.0253 (5)
N1	0.2609 (3)	0.1582 (3)	0.3520 (1)	0.0377 (6)
C2	0.1845 (3)	0.1740 (3)	0.5619 (1)	0.0252 (5)
C3	0.2676 (3)	0.1462 (3)	0.4935 (1)	0.0274 (6)
C4	0.1800 (3)	0.1892 (3)	0.4176 (1)	0.0256 (5)
C5	−0.1014 (3)	0.3193 (3)	0.3427 (1)	0.0301 (6)
C6	−0.2755 (3)	0.3835 (3)	0.3431 (1)	0.0331 (6)
C7	−0.3547 (3)	0.3987 (3)	0.4149 (1)	0.0338 (6)
C8	−0.2605 (3)	0.3519 (3)	0.4862 (1)	0.0308 (6)
C9	−0.0818 (3)	0.2865 (3)	0.4867 (1)	0.0235 (5)
C10	−0.0005 (3)	0.2666 (3)	0.4149 (1)	0.0247 (5)
C11	0.2778 (3)	0.1344 (3)	0.6448 (1)	0.0298 (6)

Table 2. *Selected geometric parameters (Å, °) for (I)*

	α phase	β phase
N1—C4	1.334 (2)	1.325 (3)
C2—C11	1.526 (2)	1.523 (3)
C11—O1	1.240 (2)	1.243 (3)
C11—O2	1.246 (2)	1.249 (2)
N1—C4—C3	120.6 (1)	120.9 (2)
N1—C4—C10	121.7 (1)	122.0 (2)
N—C2—C11	116.9 (1)	116.7 (2)
C3—C2—C11	122.4 (1)	122.8 (2)
C2—C11—O1	116.1 (1)	115.5 (2)
C2—C11—O2	116.0 (1)	116.5 (2)
O1—C11—O2	128.0 (1)	128.1 (2)
H1O—O3—H2O	103 (2)	110 (3)
H1N—N1—H2N	112 (1)	116 (2)

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
α phase				
N—H1···O3	0.90 (2)	2.02 (2)	2.889 (2)	163 (2)
N1—H1N···O2$^{\rm i}$	0.93 (2)	2.01 (2)	2.884 (2)	156 (1)
N1—H1N···O3$^{\rm ii}$	0.93 (2)	3.04 (2)	3.206 (2)	92 (1)
N1—H2N···O1$^{\rm iii}$	0.94 (2)	2.04 (2)	2.972 (2)	168 (1)
N1—H2N···O3$^{\rm ii}$	0.94 (2)	2.97 (2)	3.206 (2)	96 (1)
O3—H1O···O1$^{\rm iv}$	0.88 (3)	2.20 (3)	3.056 (2)	164 (2)
O3—H1O···O1	0.88 (3)	2.79 (2)	3.173 (2)	107 (2)
O3—H2O···O2$^{\rm v}$	0.83 (2)	2.03 (2)	2.837 (2)	162 (2)
N—H1···O1	0.90 (2)	2.38 (2)	2.681 (2)	100 (1)
β phase				
N—H1···O3	0.89 (2)	2.22 (2)	3.038 (3)	153 (2)
N1—H1N···O2$^{\rm i}$	0.90 (3)	2.02 (3)	2.877 (3)	161 (2)
N1—H2N···O1$^{\rm vi}$	0.94 (3)	2.07 (3)	2.956 (3)	158 (2)
O3—H1O···O1$^{\rm vii}$	0.86 (4)	2.11 (4)	2.959 (3)	172 (3)
O3—H2O···O2$^{\rm viii}$	0.85 (3)	2.14 (3)	2.951 (3)	161 (3)
N—H1···O1	0.89 (2)	2.32 (2)	2.668 (2)	103 (2)

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

For both phases, scan widths were $(1.60 + 0.35\tan\theta)^\circ$ in ω, with a background to scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment and the centrosymmetry indicated by the intensity statistics led to assignment of space group $P\bar{1}$ (No. 2) for the α phase and, together with systematic absences, $P2_1/c$ (No. 14) for the β phase. Fourier difference methods were used to locate the initial H-atom positions. For the α phase, solution of the non-H atoms was by *DIRDIF* (Parthasarathi, Beurskens & Slot, 1983) using the β phase molecule for orientation and translation searches. No allowance was made for extinction since the predicted coefficient was negative. The maximum peak in the final difference map occurred near the midpoint of the C2—C11 bond and the maximum negative peak occurred near the center of the heterocyclic ring. For the β phase, the maximum effect of extinction was 5.5% of F_o for $12\bar{1}$. The maximum peak in the final difference map occurred near the midpoint of the C4—C10 bond and the maximum negative peak occurred near the center of the carbocyclic ring.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structures: *DIRDIF* for the α phase; *SHELXS*86 (Sheldrick, 1985) for the β phase. For both compounds, program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

The authors thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blackburn, A. C., Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 409–411.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Okabe, N., Miura, J. & Shimosaki, A. (1996). *Acta Cryst.* C**52**, 663–665.

Parthasarathi, V., Beurskens, P. T. & Slot, H. J. B. (1983). *Acta Cryst.* A**39**, 860–864.

Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.