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Structure of Quinine Monohydrate Toluene Solvate

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(*Received* 16 *August* 1988; *accepted* 2 *November* 1988)

Abstract. $C_{20}H_{24}N_2O_2.H_2O.\frac{1}{2}C_7H_8$, $M_r = 388\cdot5$, orthorhombic, $C222_1$, $a = 10\cdot376\,(1)$, $b = 16\cdot726\,(1)$, $c = 25\cdot255\,(9)$ Å, $V = 4383$ Å^3, $Z = 8$, $D_m = 1\cdot17$, $D_x = 1\cdot177$ g cm^{-3}, Cu $K\alpha = 1\cdot5418$ Å, $\mu = 6\cdot28$ cm^{-1}, $F(000) = 1672$, $T = 295$ K, $R = 0\cdot040$, $wR = 0\cdot036$ for 2564 observed reflections. The asymmetry of the C—N bonds of the quinuclidine N atom [1·471 (4), 1·494 (4) Å], the short C—C bond of 1·356 (4) Å in the quinoline ring and the short intermolecular C···C distance between the overlapping quinoline planes [3·273 (4) Å] differentiate quinine from its derivatives and other *Cinchona* alkaloids. The water molecule, as a donor and an acceptor, connects three molecules of quinine by hydrogen bonds [O(12)···N(1) 2·867 (3), O(12)···N(2) 2·876 (2) and O(12)···O(1) 2·722 (3) Å]. The toluene and quinoline planes make a dihedral angle of 83·1 (1)° with a minimum intermolecular C···C distance of 3·648 (4) Å.

Introduction. Quinine, the best-known and perhaps the most important alkaloid of the *Cinchona* group, has several interesting pharmacological properties as an antimalarial, antibacterial and cardioactive agent. The results of the crystal structure analysis of two derivatives of quinine have been previously reported (Suszko-Purzycka, Lipińska, Piotrowska & Oleksyn, 1985;

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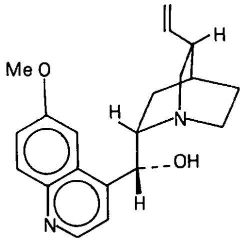
Dupont, Konsur, Lewiński & Oleksyn, 1985). This work was carried out to define the crystal and molecular structure of the quinine base.

Unlike other *Cinchona* alkaloids, *e.g.* quinidine (Kashino & Haisa, 1983), cinchonidine (Oleksyn, 1982) and cinchonine (Oleksyn, Lebioda & Ciechanowicz-Rutkowska, 1979), it was impossible to obtain quinine in pure form by simple recrystallization of the commercial product. Commercial preparations of quinine, obtained from cinchona bark, contain small amounts of other alkaloids, among them dihydroquinine (Henry, 1949; Suszko-Purzycka & Trzebny, 1964, 1965). As quinine and dihydroquinine have the same melting point, 446·5 K (Henry, 1949), it was impossible to separate them by recrystallization. Crystals of quinine obtained from many different solvents decomposed in air. The structural formula of quinine is indicated below.



Experimental. In order to eliminate the dihydro derivative, commercial quinine was subjected to purification following Thorn & Dirscherl (1935). The method is based on the difference in solubility of the dihydroquinine and the addition product of mercuric acetate to the vinyl alkaloid in aqueous ammonia. Commercial quinine purified this way was crystallized from benzene and further purified using column chromatography on Kieselgel 40 (from Merck) with particle diameters 0·63–0·20 mm. Toluene saturated with a gradually increasing amount of methanol, beginning at 100:2, was used as an eluent. The course of the column chromatography was checked using thin-layer chromatography on alumina. The alkaloid was obtained from the eluate and recrystallized from warm toluene. The colourless, transparent, prismatic crystals are stable on exposure to air, although cut crystals disintegrate completely in four weeks. The intensities were measured the first week after crystallization.

D_m measured by flotation in KI solution. Space group determined by Weissenberg photographs, crystal 0·34 × 0·30 × 0·30 mm used for diffractometer measurements, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation; cell parameters from 25 reflections in the range $10 < \theta < 17°$; 3450 reflections and antireflections collected with $2 < \theta < 58°$: index range h 0–11, k 0–18, l ±27; 2564 with $F^2 > 2\sigma(F^2)$ used in refinements. Three standard reflections measured every 1 h, no significant variation in intensity; crystal orientation checked every 200 reflections.

Structure solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). 1737 merged reflections ($R_{\rm int} = 0{\cdot}028$) used to solve structure and the full set of reflections used to refine structure. Hydrogen atoms were introduced in calculated positions ($d_{\rm C-H} = 0{\cdot}95$ Å) except H(1) of the carbinol group and H(12*A*) and H(12*B*) of the water molecule. Parameters refined: one scale factor, positional parameters of non-H atoms and H(1), H(12*A*) and H(12*B*) and anisotropic thermal parameters of non-H atoms. Thermal parameters of H atoms were not refined: $B_{\rm iso} = 5{\cdot}0$ Å^2. Full-matrix least-squares refinement of F magnitudes, $R = 0{\cdot}040$, $wR = 0{\cdot}036$, $S = 3{\cdot}50$, $w = 1/\sigma^2$; Δ/σ in the final cycle: max. 0·47 for non-H atoms, mean 0·17; max. and min. electron density in the final difference map 0·27 and −0·24 e Å^{-3} respectively; no corrections for absorption and secondary extinction. The differences between Friedel pairs of reflections were too small to define the chirality of the compound. The enantiomer was selected in agreement with references (Turner & Woodward, 1953) according to *S*, *R* conformations at atoms C(8) and C(9). Atomic scattering factors as supplied by the program, the calculations were performed with the CAD-4 *SDP* system of programs (Frenz, 1978); the equations of the least-squares planes and intermolecular distances were calculated using *GEOME* and *PLANE* (Jaskólski, 1981*a*,*b*).

Discussion. Final atomic coordinates are given in Table 1, bond distances and angles in Table 2, and hydrogen bonds in Table 3. The geometry of the molecule and the numbering scheme are illustrated in Fig. 1, overlapping of the quinoline rings in Fig. 2 and the packing diagram in Fig. 3.*

The bond lengths and angles in the bicyclic quinuclidine part of the molecule agree well with those observed in other *Cinchona* alkaloids such as derivatives of quinine and quinidine (Suszko-Purzycka *et al.*, 1985; Suszko-Purzycka, Lipińska, Karczmarzyk & Pniewska, 1987; Dupont *et al.*, 1985), quinidine (Kashino & Haisa, 1983), cinchonidine (Oleksyn, 1982) and cinchonine (Oleksyn *et al.*, 1979). However, the asymmetry of the N(1)—C(8) and N(1)—C(6) bond lengths [1·471 (4) and 1·494 (4) Å] is not marked in these related compounds. One of the bond angles at N(1) [C(8)—N(1)—C(6) 110·3 (2)°] is larger than the other two [C(2)—N(1)—C(8) 107·8 (2), C(2)—N(1)—

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51567 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
O(1)	0·2093 (2)	0·72795 (9)	0·30501 (7)	4·53 (4)
O(2)	−0·2964 (2)	0·9663 (1)	0·33258 (8)	5·28 (5)
O(12)	0·2117 (2)	0·6958 (1)	0·19937 (8)	5·61 (5)
N(1)	−0·0286 (2)	0·7051 (1)	0·38540 (9)	3·96 (5)
N(2)	0·2204 (2)	1·0292 (1)	0·30447 (9)	4·54 (5)
C(2)	−0·0840 (3)	0·7126 (2)	0·4393 (1)	4·64 (7)
C(3)	0·0211 (3)	0·7060 (2)	0·4829 (1)	4·27 (6)
C(4)	0·1476 (3)	0·6824 (2)	0·4557 (1)	4·37 (7)
C(5)	0·1234 (3)	0·6049 (2)	0·4246 (1)	5·23 (7)
C(6)	0·0273 (3)	0·6232 (2)	0·3800 (1)	4·91 (7)
C(7)	0·1898 (2)	0·7468 (2)	0·4160 (1)	4·03 (6)
C(8)	0·0731 (2)	0·7658 (1)	0·3798 (1)	3·40 (6)
C(9)	0·1091 (2)	0·7806 (1)	0·3211 (1)	3·41 (6)
C(10)	0·0354 (3)	0·7811 (2)	0·5152 (1)	5·47 (8)
C(11)	0·0315 (3)	0·7842 (2)	0·5672 (1)	7·02 (9)
C(22)	0·3048 (3)	0·9706 (2)	0·3015 (1)	4·81 (7)
C(23)	0·2722 (2)	0·8893 (2)	0·3060 (1)	4·18 (6)
C(24)	0·1476 (2)	0·8678 (1)	0·3143 (1)	3·19 (5)
C(25)	−0·0811 (2)	0·9132 (1)	0·3233 (1)	3·37 (6)
C(26)	−0·1667 (2)	0·9745 (1)	0·3258 (1)	3·79 (6)
C(27)	−0·1258 (3)	1·0548 (1)	0·3210 (1)	4·41 (6)
C(28)	0·0013 (3)	1·0710 (1)	0·3148 (1)	4·15 (6)
C(29)	0·0929 (2)	1·0085 (1)	0·3115 (1)	3·53 (6)
C(30)	0·0522 (2)	0·9289 (1)	0·31658 (9)	2·94 (5)
C(31)	−0·3429 (3)	0·8880 (2)	0·3444 (2)	7·21 (9)
C(41)	0·8022 (6)	0·500	0·500	11·4 (2)
C(42)	0·7300 (5)	0·5122 (2)	0·5459 (2)	11·7 (1)
C(43)	0·6025 (4)	0·5115 (2)	0·5447 (1)	7·9 (1)
C(44)	0·5399 (5)	0·500	0·500	7·0 (1)
C(45)	0·3935 (7)	0·500	0·500	14·1 (3)

C(6) 108·2 (3)°]. A similar pattern has been observed in related alkaloids (Suszko-Purzycka *et al.*, 1987). Compared to the compounds with *R* and *S* configurations at C(8) and C(9) (quinidine and cinchonine) where the C(2)—N(1)—C(8) angle is larger than the other two, the molecules with configurations *S* and *R* at C(8) and C(9) (quinine and cinchonidine) hence show an increased C(8)—N(1)—C(6) angle and decreased C(2)—N(1)—C(8) angle.

The bicyclic bridged rings have somewhat misshapen boat conformations, but these are less deformed than those in the hydroxy derivative of quinine (Suszko-Purzycka *et al.*, 1985). This is shown by the somewhat smaller values of the torsion angles around the non-bonded line N(1)···C(4). The values (with those for the derivative in square brackets) are: C(2)—N(1)···C(4)—C(3) −4·5 (2) [−5·76 (2)], C(8)—N(1)···C(4)—C(3) −8·2 (3) [−11·72 (2)] and C(6)—N(1)···C(4)—C(5) −5·4 (2)° [−7·98 (2)°].

The skew conformation of the molecule is somewhat different from that in the hydroxy derivative of quinine (Suszko-Purzycka *et al.*, 1985). Comparison of the torsion angles (with those of the derivative, given below in square brackets) indicate smaller differences between those around C(9)—C(24) than those around C(8)—C(9). The torsion angles are: C(8)—C(9)—C(24)—C(30) −72·0 (3) [−79·0 (2)], C(8)—C(9)—C(24)—C(23) 108·1 (3) [101·0 (2)], O(1)—C(9)—

Table 2. *Bond distances* (Å) *and angles* (°)

O(1)—C(9)	1·422 (3)	C(9)—C(24)	1·522 (4)
O(2)—C(26)	1·363 (3)	C(10)—C(11)	1·317 (5)
O(2)—C(31)	1·427 (4)	C(22)—C(23)	1·406 (4)
N(1)—C(2)	1·484 (4)	C(23)—C(24)	1·358 (3)
N(1)—C(6)	1·494 (3)	C(24)—C(30)	1·424 (4)
N(1)—C(8)	1·471 (4)	C(25)—C(26)	1·358 (3)
N(2)—C(22)	1·317 (3)	C(25)—C(30)	1·418 (3)
N(2)—C(29)	1·379 (3)	C(26)—C(27)	1·413 (3)
C(2)—C(3)	1·553 (4)	C(27)—C(28)	1·356 (4)
C(3)—C(4)	1·534 (4)	C(28)—C(29)	1·415 (3)
C(3)—C(10)	1·504 (4)	C(29)—C(30)	1·404 (3)
C(4)—C(5)	1·537 (4)	C(41)—C(42)	1·395 (5)
C(4)—C(7)	1·536 (4)	C(42)—C(43)	1·324 (7)
C(5)—C(6)	1·535 (4)	C(43)—C(44)	1·317 (5)
C(7)—C(8)	1·549 (4)	C(44)—C(45)	1·519 (9)
C(8)—C(9)	1·550 (4)		

C(26)—O(2)—C(31)	116·9 (2)	C(7)—C(8)—C(9)	114·1 (2)
C(2)—N(1)—C(6)	108·2 (3)	O(1)—C(9)—C(8)	110·6 (2)
C(2)—N(1)—C(8)	107·8 (2)	O(1)—C(9)—C(24)	111·7 (2)
C(6)—N(1)—C(8)	110·3 (2)	C(8)—C(9)—C(24)	108·9 (2)
C(22)—N(2)—C(29)	117·3 (3)	C(3)—C(10)—C(11)	124·8 (3)
N(1)—C(2)—C(3)	111·9 (3)	N(2)—C(22)—C(23)	123·8 (2)
C(2)—C(3)—C(4)	107·6 (2)	C(22)—C(23)—C(24)	119·8 (2)
C(2)—C(3)—C(10)	113·2 (2)	C(9)—C(24)—C(23)	121·4 (3)
C(4)—C(3)—C(10)	111·9 (2)	C(9)—C(24)—C(30)	120·0 (2)
C(3)—C(4)—C(5)	107·9 (2)	C(23)—C(24)—C(30)	118·6 (3)
C(3)—C(4)—C(7)	110·8 (3)	C(26)—C(25)—C(30)	120·3 (3)
C(5)—C(4)—C(7)	107·7 (2)	O(2)—C(26)—C(25)	125·2 (2)
C(4)—C(5)—C(6)	108·2 (2)	O(2)—C(26)—C(27)	113·7 (2)
N(1)—C(6)—C(5)	111·7 (2)	C(25)—C(26)—C(27)	121·1 (2)
C(4)—C(7)—C(8)	107·8 (3)	C(26)—C(27)—C(28)	119·5 (2)
N(1)—C(8)—C(7)	111·2 (2)	C(27)—C(28)—C(29)	120·8 (2)
N(1)—C(8)—C(9)	111·9 (3)	N(2)—C(29)—C(28)	117·8 (3)
N(2)—C(29)—C(30)	122·6 (3)	C(25)—C(30)—C(29)	118·7 (3)
C(28)—C(29)—C(30)	119·6 (2)	C(41)—C(42)—C(43)	121·2 (5)
C(24)—C(30)—C(25)	123·5 (2)	C(42)—C(43)—C(44)	120·8 (4)
C(24)—C(30)—C(29)	117·9 (3)	C(43)—C(44)—C(45)	119·5 (3)

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°)

O—H···*A*	O—H	H···*A*	O···*A*	O—H···*A*
O(12^{i})—H(12*A*)···N(2^{iii})	0·953 (17)	1·956 (19)	2·876 (2)	162 (2)
O(12^{i})—H(12*B*)···N(1^{ii})	0·907 (29)	1·966 (28)	2·867 (3)	171 (2)
O(1^{i})—H(1)···O(12^{i})	0·986 (25)	1·757 (26)	2·722 (3)	165 (2)

Equivalent positions: (i) x, y, z; (ii) $-x, y, 0·5-z$; (iii) $0·5-x, 0·5+y, 0·5-z$.

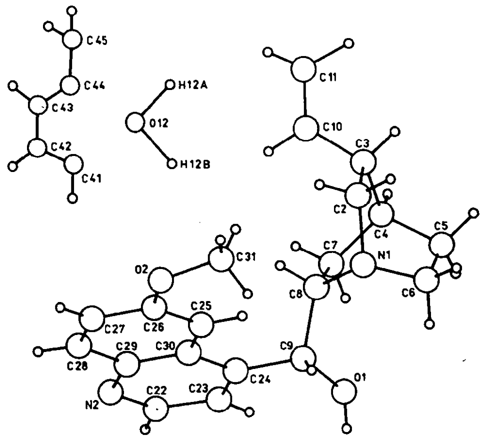

Fig. 1. The molecular structure of quinine illustrating the atomic numbering scheme.

C(24)—C(23) −14·3 (3) [−21·2 (2)], C(7)—C(8)—C(9)—C(24) −85·1 (2) [−67·2 (2)], N(1)—C(8)—C(9)—O(1) −89·5 (2) [−71·9 (2)], C(7)—C(8)—C(9)—O(1) 37·9 (2)° [55·8 (2)°].

The quinoline ring is planar to within 0·018 (2) Å with the O(2) atom lying in the plane [distance 0·006 (2) Å] and C(31) being displaced by −0·164 (4) Å out of the plane. The bond lengths and angles in the quinoline part of the molecule are in good agreement with corresponding values in other alkaloids containing the methoxyquinoline ring such as derivatives of quinine and quinidine (Suszko-Purzycka *et al.*, 1985; Suszko-Purzycka *et al.*, 1987; Dupont *et al.*, 1985), and quinidine base (Kashino & Haisa, 1983). The only exception is the C(26)—C(27) bond length of 1·356 (4) Å, which is somewhat short when compared with the average value of 1·410 (6) Å found in the above-cited compounds. The shortening probably results from interaction between adjacent quinoline rings in the crystal. The quinoline rings, related by the twofold axis parallel to **b**, overlap each other with a short intermolecular distance of 3·273 (4) Å [C(28)···C(28′)]. The planes make a dihedral angle of 5·8°. The distances between certain atoms and the least-squares plane of the neighbouring ring are: 3·231 (3) for C(28), 3·318 (3) for C(29), 3·386 (2) for O(2), 3·375 (3) for C(26) and 3·461 (2) Å for C(30) (Fig. 2).

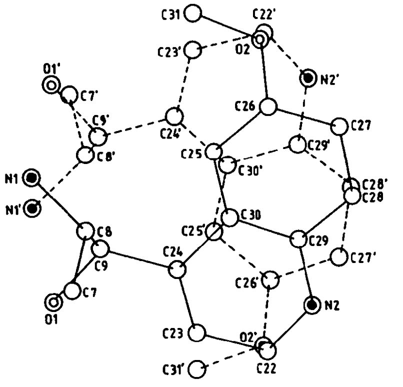

Fig. 2. Overlapping of the quinoline rings, viewed down the *c* axis.

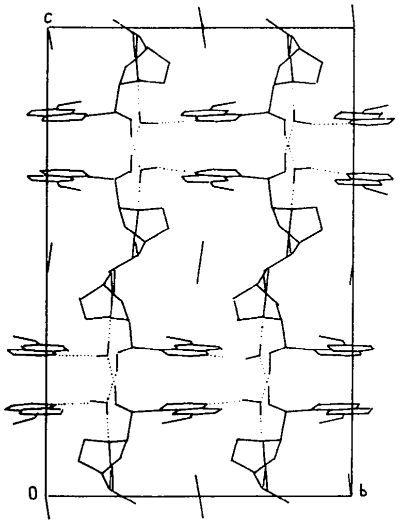

Fig. 3. Packing diagram. H atoms are omitted except those of the water molecule and carbinol group. Hydrogen bonds are shown as dotted lines.

The molecular packing in the crystal is also determined by the presence of the water molecule, which forms strong hydrogen bonds connecting three adjacent molecules of quinine by N(1), N(2) and O(1). Each water molecule exhibits both donor and acceptor functions. The geometry of the hydrogen bonds is given in Table 3 and shown in Fig. 3.

The toluene lies in special positions along the twofold axis parallel to **a**. The molecules of toluene are fixed in channels formed by the network of hydrogen bonds and pairs of quinuclidine and quinoline rings. The quinoline and toluene planes form a dihedral angle of 83·1 (1)°. Minimum distances between the toluene and the quinine molecules are 3·648 (4) and 3·682 (3) Å for C(29)···C(43) and C(10)···C(44) respectively. The packing of the molecules is shown in Fig. 3.

The measurements and calculations were carried out at the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw. We thank Dr Kinga Suwińska for her assistance. This research was supported by Project RP.II.10 from PME.

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Azoles. 19.* Structure of 4-Nitro-7-phenylsulfonylmethylindazole

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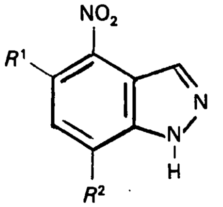
(*Received* 26 *January* 1988; *accepted* 30 *September* 1988)

Abstract. $C_{14}H_{11}N_3O_4S$, $M_r = 317{\cdot}17$, monoclinic, $P2_1/n$, $a = 7{\cdot}842\,(1)$, $b = 13{\cdot}292\,(4)$, $c = 13{\cdot}734\,(3)$ Å, $\beta = 95{\cdot}47\,(1)°$, $V = 1425{\cdot}2\,(6)$ Å^3, $D_m = 1{\cdot}48\,(1)$, $D_x = 1{\cdot}48$ Mg m^{-3}, $Z = 4$, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo}\,K\alpha) = 0{\cdot}201$ mm^{-1}, $F(000) = 656$, room temperature, final $R = 0{\cdot}035$ for 1647 observed reflections. The indazole system is strictly planar. The nitro group makes with it a dihedral angle of 2·0 (1)°. The phenyl ring of the phenylsulfonylmethyl substituent is turned by 13·4 (1)° out of the plane of the indazole system.

Introduction. The compound examined in this work was obtained by the action of chloromethyl phenyl sulfone on 4-nitroindazole. This reaction proceeds according to the mechanism of the vicarious nucleophilic substitution of hydrogen (Makosza, Kinowski, Danikiewicz & Mudryk, 1986). In this reaction the substitution takes place in *ortho* and/or *para* position(s) to the nitro group. Hence the product obtained can assume two different structures, *i.e.* (2) or (2*a*). It was not possible to determine the exact position of the newly introduced phenylsulfonylmethyl group on the basis of the analysis of the ^{1}H NMR spectrum, since its doublets at $\delta = 8{\cdot}08$ and 7·30 (both with the coupling constant of $J = 8$ Hz) might be attributed to two different pairs of hydrogen atoms in *ortho* position, *i.e.* 5 and 6 [compound (2)] or 6 and 7 [compound (2*a*)]. Unsuccessful attempts to obtain an *N*-acetyl derivative of the compound analyzed suggested structure (2) (Dudzińska-Usarewicz, Wrzeciono, Frankiewicz, Linkowska, Köhler & Nuhn, 1987). These suppositions were supported by X-ray analysis.



	R^1	R^2
(2)	H	$C_6H_5SO_2CH_2$
(2a)	$C_6H_5SO_2CH_2$	H

Experimental. Yellow prismatic crystals recrystallized from methanol, D_m by flotation, crystal dimensions $0{\cdot}55 \times 0{\cdot}5 \times 0{\cdot}25$ mm, Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from least-squares treatment of setting angles of 15 reflections with $18° \leq 2\theta \leq 27°$, θ–2θ scan technique, $2\theta \leq 48°$, two standard reflections monitored every 100 reflections, no significant intensity variation, no absorption correction, profiles measured for 2646 reflections, 2155 unique reflections, $R_{\text{int}} = 0{\cdot}044$, range of hkl: h −8→8, k 0→14, l 0→15, profile analysis according to Lehmann & Larsen (1974), 1647 reflections with $I \geq 1{\cdot}96\sigma(I)$ considered observed and used in the refinement, structure solved by direct methods using *SHELX76* (Sheldrick, 1976), refinement on F by full-matrix least-squares method, refined $N = 244$ parameters, anisotropic non-H atoms, H atoms generated from ΔF map and refined as isotropic, $w^{-1} = \sigma^2(F)$, empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c(1 - xF/\sin\theta)$, x converged at 0·005 (1), final $R = 0{\cdot}035$ and $wR = 0{\cdot}033$, $S = 2{\cdot}613$, $(\Delta/\sigma)_{\max} = 0{\cdot}05$, max. and min. height in the final ΔF map: 0·15 and −0·20 e Å^{-3}; computer programs: *SHELX76* (Sheldrick, 1976) and

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* Part 18: Dudzinska-Usarewicz, Wrzeciono, Frankiewicz, Linkowska, Kohler & Nuhn (1987).

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