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Methyl *β*-D-Galactopyranoside*

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Abstract. $C_7H_{14}O_6$, M_r = 194·19, orthorhombic, $P2_12_12_1$, a = 7·774 (1), b = 8·530 (1), c = 13·126 (1) Å [λ(Cu $K\alpha_1$) = 1·54051 Å], V = 870·41 Å^3, Z = 4, D_m = 1·485, D_x = 1·482 g cm^{-3}. The structure was solved with *MULTAN* and refined to $R(F_o)$ = 0·025 for 1086 reflections measured with Cu $K\alpha$ radiation. The glycosidic bond length, C(1)—O(1), is 1·390 Å and the ring O valence angle, C(5)—O(5)—C(1), is 111·1°. These values are significantly smaller than those observed in methyl *α*-D-galactopyranoside: 1·405 Å and 113·8° respectively. The conformation of the primary hydroxyl group is *gauche–trans* and the pyranose ring is the normal chair ($^4C_1$). Three of the hydroxyl groups are involved in an infinite chain of strong hydrogen bonds. The fourth forms a weak asymmetric bifurcated hydrogen bond to the ring and glycosidic O atoms.

Introduction. The objective of this study was to compare the molecular dimensions and hydrogen-bond structure of the title compound (I) with those of the corresponding *α*-compound (II) (Gatehouse & Poppleton, 1971). (I) was obtained from the Sigma Chemical Co. Suitable crystals were grown by slow evaporation of a 95% ethanol–water solution at room temperature. The systematic absences and the diffraction symmetry determined the space group, $P2_12_12_1$. The cell constants were obtained by least-squares refinement of the setting angles of 25 reflections with 110° < 2θ < 128°.

A crystal of dimensions 0·14 × 0·26 × 0·37 mm was used for the data collection with graphite-monochromated Cu $K\alpha$ radiation on a CAD-4 automatic diffractometer. The 4644 reflections in the hkl, $\bar{h}kl$, $h\bar{k}l$ and $\bar{h}\bar{k}l$ octants were measured by θ–2θ scans to 2θ = 156°. Absorption corrections were made with the program *ABSOR* (Templeton & Templeton, 1973), with a linear absorption coefficient for Cu $K\alpha$ of 10·83 cm^{-1}. The minimum and maximum corrections to F_o^2 were 1·13 and 1·30, respectively. The symmetry-related measurements were then averaged to give 1086 independent reflections, of which six had $F_o^2 < 0$. The R factor between symmetry-equivalent intensities was 0·021.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971), with 150 reflections with $E \geq$ 1·42 used for phase generation. Refinement was by full-matrix least squares with *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962) to minimize $\Sigma\,\omega|F_o - kF_c|^2$, with $\omega^{-1} = [\sigma_c^2(F_o^2) + (0{\cdot}004F_o^2)^2]/4F_o^2$, where σ_c is from counting statistics. The H atoms were located from a difference synthesis. The non-hydrogen and H atom parameters were refined anisotropically

Table 1. *Fractional atomic coordinates* (×10^4) *for non-hydrogen atoms*

Estimated standard deviations given in parentheses refer to the least significant digit.

	x	y	z
C(1)	1644 (2)	5370 (2)	9163 (1)
C(2)	197 (2)	6571 (2)	9231 (1)
C(3)	156 (2)	7548 (2)	8260 (1)
C(4)	1921 (2)	8215 (2)	8002 (1)
C(5)	3244 (2)	6893 (2)	7998 (1)
C(6)	5042 (2)	7489 (2)	7788 (1)
C(7)	2730 (4)	3176 (3)	10029 (2)
O(1)	1782 (2)	4600 (1)	10093 (1)
O(2)	−1430 (2)	5813 (2)	9319 (1)
O(3)	−1107 (2)	8746 (2)	8301 (1)
O(4)	2361 (1)	9401 (1)	8723 (1)
O(5)	3242 (1)	6133 (1)	8977 (1)
O(6)	6225 (2)	6226 (2)	7711 (1)

Table 2. *Fractional atomic coordinates* (×10^3), *isotropic thermal parameters* (Å^2) *and bond distances* (Å) *for the hydrogen atoms*

	x	y	z	B(iso)	
H(C1)	138 (2)	463 (2)	863 (1)	2·5 (4)	0·96 (2)
H(C2)	43 (2)	719 (2)	981 (1)	2·3 (4)	0·94 (2)
H(C3)	−11 (3)	684 (3)	770 (1)	2·7 (4)	0·97 (2)
H(C4)	187 (2)	871 (2)	733 (1)	2·1 (3)	0·98 (2)
H(C5)	294 (2)	609 (2)	749 (1)	2·8 (4)	0·98 (2)
H(C61)	505 (2)	802 (2)	712 (1)	2·5 (4)	0·99 (2)
H(C62)	540 (2)	825 (2)	833 (1)	2·7 (4)	1·00 (2)
H(C71)	258 (4)	262 (3)	1067 (3)	7·1 (8)	0·97 (3)
H(C72)	394 (5)	332 (4)	981 (3)	8·8 (9)	0·99 (4)
H(C73)	241 (4)	251 (4)	952 (3)	7·8 (9)	0·91 (4)
H(O2)	−170 (3)	573 (3)	988 (2)	4·2 (5)	0·77 (3)
H(O3)	−123 (4)	907 (3)	892 (2)	6·6 (8)	0·86 (3)
H(O4)	295 (3)	1011 (3)	841 (2)	4·0 (5)	0·86 (2)
H(O6)	682 (4)	610 (3)	824 (2)	5·7 (7)	0·84 (3)

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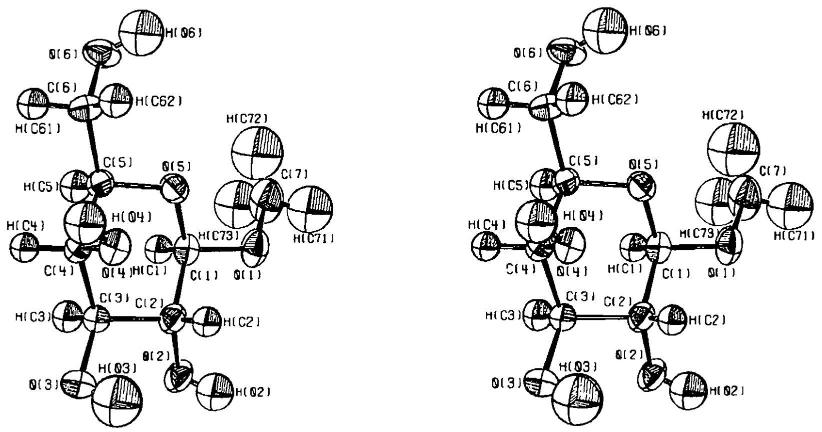

Fig. 1. Stereoview of the molecule showing the conformation and atomic notation. Thermal ellipsoids at 50% probability (Johnson, 1976).

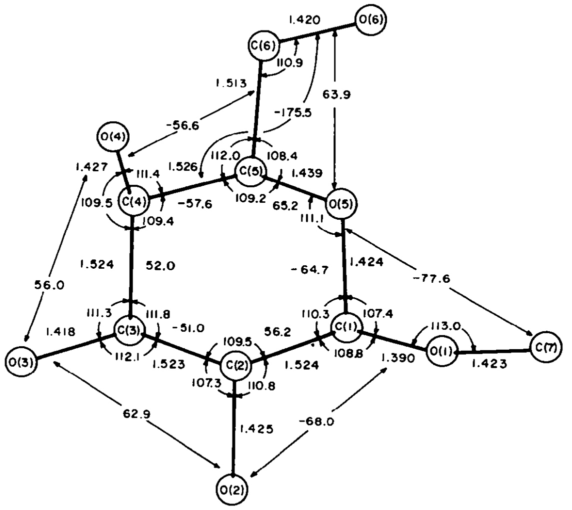

Fig. 2. Molecular dimensions (Å and degrees).

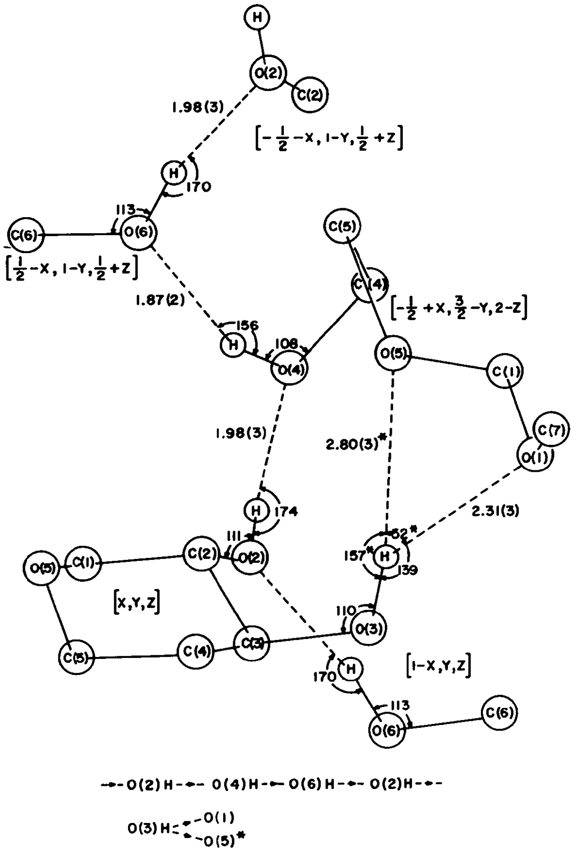

Fig. 3. Hydrogen-bonding structure.

and isotropically respectively, together with a Zachariasen isotropic extinction parameter (Coppens & Hamilton, 1970), which refined to 0·86 (8) × 10^4. The final R (= $\Sigma\, |F_o - kF_c|/\Sigma\, |F_o|$) and R_ω [= $(\Sigma\, \omega |F_o - kF_c|^2/\Sigma\, \omega |F_o|^2)^{1/2}$] for 1086 reflections were 0·025 and 0·031 respectively.

The atomic scattering factors for O and C were those tabulated by Doyle & Turner (1968) and those for H were given by Stewart, Davidson & Simpson (1965). The final positional parameters are given in Tables 1 and 2.* The conformation and the atomic numbering are shown in Fig. 1. The molecular dimensions for non-hydrogen atoms are reported in Fig. 2; the σ's for the bond lengths and angles are 0·002 Å and 0·1°, respectively [except 0·003 Å for C(7)—O(1)].

The C—H and O—H bond distances and their estimated standard deviations are included in Table 2. A rigid-body-motion analysis (Schomaker & Trueblood, 1968) showed the rigid-body approximation to be good.* Thermal motion corrections would lengthen the C—C bonds by 0·005 Å and the C—O bonds by 0·004 Å over the uncorrected values shown in Fig. 2.

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* Lists of structure factors, atomic thermal parameters and results of rigid-body-motion analysis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32844 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* See previous footnote.

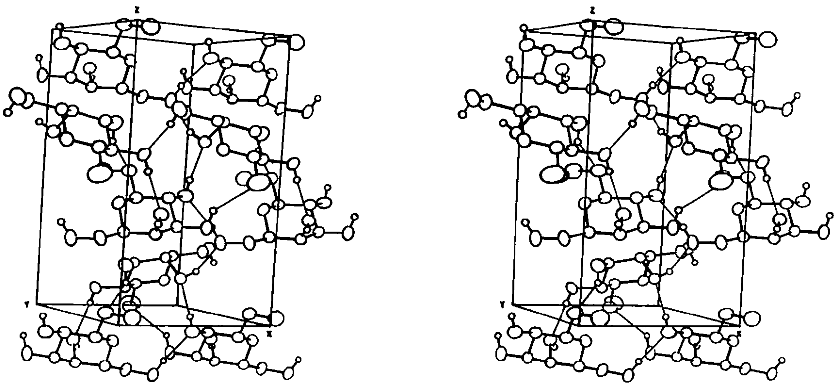
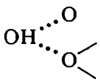


Fig. 4. Stereoview of the unit-cell contents (*c* axis vertical).

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

···OH···OH···	H···O	$H\cdots O_{corr}$*	O···O	$\angle O{-}H\cdots O_{corr}$*
O(2)H(O2)···O(4)[$-\frac{1}{2}+x, \frac{3}{2}-y, 2-z$]	1·98	1·79	2·743 (2)	173
O(4)H(O4)···O(6)[$1-x, \frac{1}{2}+y, \frac{3}{2}-z$]	1·87	1·78	2·679 (2)	156
O(6)H(O6)···O(2)[$1+x, y, z$]	1·98	1·86	2·811 (2)	169
				
O(3)H(O3)···O(1)[$-\frac{1}{2}+x, \frac{3}{2}-y, 2-z$]	2·31	2·24	3·021 (2)	138
···O(5)[$-\frac{1}{2}+x, \frac{3}{2}-y, 2-z$]	2·80	2·71	3·610 (2)	157

* Corrected by expanding the covalent O—H bond distances to the neutron diffraction value of 0·96 Å in the direction of the bond.

Discussion. The galactopyranose ring is the normal $^4C_1$ chair, with a ring distortion which is greater than that in the structure of (II) (Gatehouse & Poppleton, 1971), where the ring torsion angles lie in the range of 52·2 to 61·5°. This greater distortion is also shown by the puckering parameters, as defined by Cremer & Pople (1975), which are $q_2 = 0{\cdot}062$, $q_3 = 0{\cdot}580$, $Q = 0{\cdot}583$ Å, $\theta = 6{\cdot}1$, $\varphi_2 = 347{\cdot}9°$ for (I), as compared with $q_2 = 0{\cdot}045$, $q_3 = 0{\cdot}562$, $Q = 0{\cdot}564$ Å, $\theta = 4{\cdot}6$, $\varphi_2 = 279{\cdot}1°$ for (II). It was not expected that the molecule of (I), with only one axial substituent to the ring, would have a more distorted pyranose ring than that of (II), which has two axial substituents. It is even more surprising to discover that this is a general property of α- and β-pyranose molecules (Jeffrey & Takagi, 1977). The conformational angles of the primary alcohol group for β and α compounds are 63·9 and 62·6° respectively, *i.e.* both are *gauche–trans*. The torsion angle of the glycosidic bond C(1)—O(1) for (I) is −77·6°; for (II) this angle is 63·5° (Gatehouse & Poppleton, 1971). In the acetal bond sequence, C(5)—O(5)—C(1)—O(1)—C(7), the two ring bonds show only a small difference in bond lengths, 0·015 Å, and the glycosidic bond, C(1)—O(1), is short, 1·390 Å. For (II), C(1)—O(1) is 1·405 Å and the ring bond lengths differ by 0·021 Å. The valence-bond angles in the sequence C(5)—O(5)—C(1)—O(1) are smaller in (I) than in (II); *i.e.* 111·1 and 107·4° *versus* 113·8 and 111·3°. This is a characteristic structural difference between the α- and β-pyranose molecules, as pointed out by Arnott & Scott (1972) and by Jeffrey & Takagi (1977). These differences in bond lengths and valence angles for the C—O ring and glycosidic bonds agree well with the predictions of Jeffrey, Pople & Radom (1972, 1974) and Jeffrey, Pople, Binkley & Vishveshwara (1978), based on *ab initio* 431G-basis-set molecular-orbital calculations on model compounds.

The C—C bond lengths and the exocyclic C—O bond lengths agree in the molecules of (I) and (II) within the sum of the standard deviations (0·007 Å), except for C(3)—O(3), where the difference is 0·028 Å.

The hydrogen bonding in (I) consists of an infinite chain of strong bonds, ···O(2)H···O(4)H···O(6)H···O(2)H···, and a weak asymmetric bifurcated interaction between O(3)H and the two acetal O atoms O(1) and O(5) at 2·31 and 2·80 Å. A similar asymmetric bifurcated hydrogen bond has been observed by neutron diffraction in β-D-fructopyranose by Takagi & Jeffrey (1977), except that the bonds are stronger, 1·965 and 2·349 Å. The hydrogen-bonding scheme is shown in Fig. 3 and in the stereoview of the unit-cell contents given in Fig. 4.

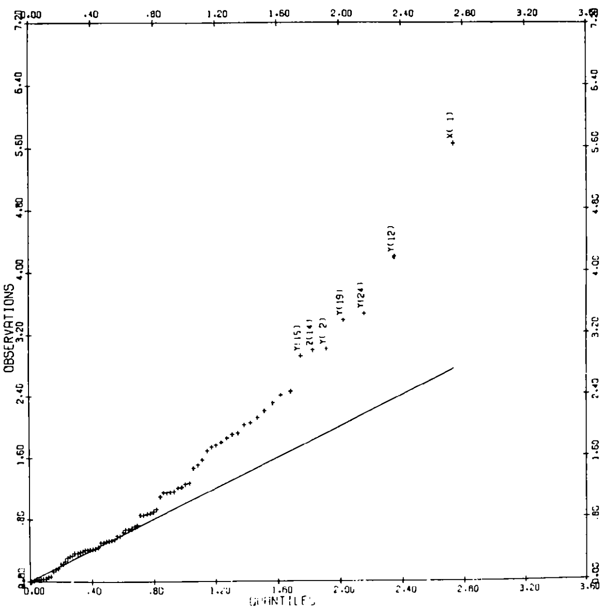


Fig. 5. Half-normal distribution plot.

The hydrogen-bond distances and angles are given in Table 3, with the covalent O—H distances normalized to the neutron diffraction value of 0·96 Å by moving the H atom in the direction of the O—H bond. The corrected H···O distances for hydrogen bonds between the hydroxyl groups involved in donor–acceptor interactions range from 1·78 to 1·86 Å. This distribution is similar to that reported for neutron diffraction studies of related methyl pyranosides (Jeffrey, Gress & Takagi, 1977; Poppleton, Jeffrey & Williams, 1975; Jeffrey, McMullan & Takagi, 1977).

The distances between O(3)H and the two acetal-type O atoms, O(5) and O(1), lie between that of the asymmetric bifurcated interaction in β-D-fructopyranose (Takagi & Jeffrey, 1977) and the *non-bonded* interactions observed in methyl α-D-glucopyranoside (Berman & Kim, 1968; Jeffrey, McMullan & Takagi, 1977) and in sucrose (Brown & Levy, 1973). In the methyl α-D-glucopyranoside structure there are two long H···O distances (2·328, 2·633 Å) and in sucrose there are three (2·309, 2·534 and 2·539 Å). With the additional evidence now available from this structure and from that of β-D-fructopyranose (Takagi & Jeffrey, 1977), we consider these interactions to be weak bifurcated and trifurcated electrostatic interactions of the hydrogen-bond type, rather than 'non-bonding' interactions of the van der Waals type. This question is discussed in more detail elsewhere (Jeffrey & Takagi, 1978).

Note added in proof: Since the acceptance of this paper, a report of the structure determination of methyl β-D-galactopyranoside has been published (Sheldrick, 1977).

The half-normal distribution plot (Abrahams & Keve, 1971) of the two sets of atomic positional parameters is shown in Fig. 5. It has some curious features. Of the 81 parameters, 42 lie on the line of slope unity, indicating that the estimated standard deviations are correct in both structures. The next 32 parameters lie on a slope of 1·5 and there are seven outliers. These are not entirely the hydrogen parameters, as might be expected, but include C(1)x, O(5)y, C(2)y. These underestimates of the parameter errors are reflected in differences in the C(1)—O(1), C(1)—O(5), C(2)—O(2) bond lengths of greater than 1σ, *i.e.* 0·010 (2·2 σ), 0·012 (2·7σ), 0·011 Å (2·0 σ), respectively.

One or both of the analyses have some systematic errors. We believe that our report is the more accurate for the following reasons: (i) the intensities were measured in all four octants; (ii) absorption corrections were applied; (iii) the agreement between symmetry-equivalent reflections after absorption correction was $R = 0{\cdot}021$; (iv) the final R and R_ω values were 0·025 and 0·031 for 1086 symmetry-averaged reflections (*versus* 0·040 for 917 reflections measured in one octant).

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2,2′-Dihydroxy-7,7,7′,7′-tetramethyl-*exo*-2,2′-bi{3,4-benzo-9-oxabicyclo[3.3.1]non-3-enyl}

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Abstract. $C_{28}H_{34}O_4$, orthorhombic, *Fdd*2, a = 22·771 (14), b = 19·135 (11), c = 10·308 (5) Å, 23 °C; M_r = 434·58, Z = 8, D_x = 1·285 g cm^{-3}; the material was crystallized from acetone at room temperature. The molecule is located about a twofold axis; the two equivalent halves of the molecule are joined by a single C—C bond and by intramolecular hydrogen bonds.

Introduction. As an adjunct to continuing research on the photochemistry of cyclic dienones (see, for example, Hart & Suzuki, 1975*a*,*b*,*c*), irradiation of 7,7-dimethyl-3,4-benzo-9-oxabicyclo[3.3.1]non-3-en-2-one in cyclohexane through Pyrex gave a dimeric product for which attempts to elucidate its structure by use of IR, UV, and NMR spectra were not successful (Suzuki, 1975). The crystal and molecular structure determination of the title compound was undertaken to identify it.

Table 1. *Atomic parameters*

Fractional coordinates are × 10^4, except those for hydrogen atoms, which are × 10^3.

	x	y	z	B_{iso}(Å^2)
C(1)	5606 (1)	9659 (2)	6339 (5)	
C(2)	5226 (1)	9681 (2)	5104*	
C(3)	5646 (1)	9735 (2)	3962 (5)	
C(4)	6206 (1)	10012 (2)	4153 (5)	
C(5)	6416 (1)	10247 (2)	5468 (5)	
C(6)	6886 (2)	9782 (2)	6081 (6)	
C(7)	6624 (1)	9194 (2)	6920 (5)	
C(8)	6007 (1)	9020 (2)	6403 (5)	
O(9)	5932 (1)	10299 (1)	6360 (4)	
C(10)	5493 (2)	9479 (2)	2741 (5)	
C(11)	5885 (2)	9517 (2)	1721 (5)	
C(12)	6432 (2)	9805 (2)	1901 (5)	
C(13)	6589 (2)	10042 (2)	3097 (5)	
C(14)	6587 (2)	9409 (3)	8345 (5)	
C(15)	7014 (2)	8549 (3)	6834 (6)	
O(16)	4923 (1)	9035 (1)	4973 (4)	
H(1)	535 (1)	971 (1)	709 (3)	0·9 (5)
H(2)	656 (1)	1071 (2)	540 (3)	2·0 (6)
H(3)	717 (2)	1007 (2)	660 (4)	3·8 (8)
H(4)	713 (2)	957 (2)	536 (4)	3·9 (8)
H(5)	582 (1)	869 (2)	699 (3)	2·2 (6)
H(6)	606 (1)	882 (2)	548 (4)	3·4 (8)
H(7)	509 (2)	926 (2)	260 (4)	3·9 (8)
H(8)	577 (1)	934 (2)	89 (4)	3·3 (8)
H(9)	670 (2)	981 (2)	110 (4)	4·8 (9)
H(10)	698 (2)	1025 (2)	323 (3)	3·1 (7)
H(11)	641 (2)	903 (2)	891 (4)	4·6 (9)
H(12)	633 (2)	984 (3)	841 (4)	5·4 (10)
H(13)	696 (2)	952 (2)	869 (4)	5·7 (11)
H(14)	701 (2)	839 (2)	602 (5)	5·3 (11)
H(15)	688 (2)	814 (3)	741 (5)	6·9 (13)
H(16)	742 (2)	867 (2)	700 (4)	4·2 (8)
H(17)	459 (2)	910 (2)	543 (4)	5·3 (12)

* Parameter held constant during refinement.

A single crystal of approximate dimensions 0·2 × 0·2 × 0·2 mm [μ(Mo $K\alpha$) = 0·47 cm^{-1}] was used. The diffraction conditions hkl: $h + k$, $k + l$, $(l + h) = 2n$, $h0l$: $h + l = 4n$, $0kl$: $k + l = 4n$, the absence of other unrelated conditions, and the orthorhombic symmetry establish the space group as *Fdd*2 (No. 43). Diffraction data were measured at 23 °C with a Picker FACS-I automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation. The cell parameters were determined by a least-squares fit to the angular settings ($2\theta,\omega,\chi,\varphi$) of 12 reflections in the range $35° \leq 2\theta \leq 40°$ for which the α_1,α_2 doublet was clearly resolved [λ(Mo $K\alpha_1$) = 0·70926 Å]. The 1371 unique reflections (including 256 'unobserved') in the $-h+k+l$ octant were collected for $2\theta \leq 55°$ using the θ–2θ scan method [scan speed 1° (2θ) min^{-1}; 10 s backgrounds; scan range of 1·0° (2θ) plus the α_1–α_2 divergence; and three standard reflections measured after every 100 data were used to scale the data]. The data were reduced and standard deviations calculated as a function of counting statistics as reported previously (Wei & Ward, 1976); the least-squares-refinement weights were calculated from the standard deviations of the structure factors by w =