the conformation with this angle nearly 90 or 270° is unstable and shows the highest energy level.

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Structure of the Neuroleptic Drug 4-Amino-*N*-1-[(1-ethyl-2-pyrrolidinyl)methyl]-5-(ethylsulfonyl)-2-methoxybenzamide (Amisulpride)

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Abstract. $C_{17}H_{27}N_3O_4S$, $M_r = 369{\cdot}48$, monoclinic, $P2_1/c$, $a = 13{\cdot}333\,(7)$, $b = 7{\cdot}946\,(4)$, $c = 17{\cdot}550\,(10)$ Å, $\beta = 96{\cdot}99\,(4)°$, $V = 1845\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}33$, $D_x = 1{\cdot}330$ Mg m^{-3}, graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å, $\mu = 1{\cdot}744$ mm^{-1}, $F(000) = 792$, $T = 293$ K. Final $R = 0{\cdot}038$ for 2405 unique observed reflections. The folded conformation of the molecule with the least-squares planes of the aromatic and the pyrrolidine rings almost perpendicular is essentially determined by intra- and intermolecular hydrogen bonds. In this way, two pseudorings are formed, one linking the amide H with the methoxy O, and a second one involving the 4-amino H and a sulfonyl O. An intermolecular hydrogen bond forces the planar amide group some 28° out of the plane of the aromatic ring.

Introduction. Amisulpride belongs to the same class of neuroleptics as the widely reputed sulpiride. These drugs act by blocking the dopamine D_2 receptor (Kebabian & Calne, 1979). The present investigation is part of a study examining the structural requirements for doing so.

Experimental. Colorless crystals from a methanol–amyl acetate solution, 0·6 × 0·2 × 0·2 mm. Density measured by flotation in *n*-heptane/CCl_4, systematic absences from Weissenberg photographs. Siemens AED2 diffractometer, cell constants by least-squares refinement of the setting angles of 44 reflections with $35 < 2\theta < 55°$, ω/θ scan, $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}5840$ Å^{-1}, $0 \le h \le 16$, $0 \le k \le 9$, $-21 \le l \le 21$. Intensities of four standard reflections (020, 400, 004, 100) monitored every hour showed only statistical fluctuations, 3530 reflections measured, 2405 observed reflections with $|F_o| > 6|\sigma(F_o)|$. Data reduction with Stoe &

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors* ($Å^2 \times 10^4$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} ($Å^2$)
C(1)	0·5688 (2)	0·2185 (3)	−0·0880 (1)	338 (5)
C(2)	0·5123 (2)	0·2459 (3)	−0·0259 (1)	341 (5)
C(3)	0·5525 (2)	0·2062 (3)	0·0485 (1)	384 (5)
C(4)	0·6480 (2)	0·1325 (3)	0·0650 (1)	365 (5)
C(5)	0·7053 (2)	0·1092 (3)	0·0032 (1)	365 (5)
C(6)	0·6648 (2)	0·1548 (3)	−0·0712 (1)	352 (5)
C(7)	0·5329 (2)	0·2573 (3)	−0·1709 (1)	347 (5)
N(8)	0·4349 (1)	0·2505 (3)	−0·1939 (1)	447 (5)
C(9)	0·3925 (2)	0·2846 (4)	−0·2725 (1)	475 (6)
C(10)	0·2817 (2)	0·3266 (4)	−0·2787 (1)	500 (6)
C(11)	0·2556 (2)	0·4726 (4)	−0·2264 (2)	695 (9)
C(12)	0·1562 (3)	0·4279 (5)	−0·2009 (2)	883 (11)
C(13)	0·1222 (2)	0·2665 (4)	−0·2439 (2)	623 (8)
N(14)	0·2171 (1)	0·1885 (3)	−0·2579 (1)	450 (5)
C(15)	0·2024 (2)	0·0611 (4)	−0·3203 (1)	571 (8)
C(16)	0·1369 (2)	−0·0829 (5)	−0·3019 (2)	699 (9)
O(17)	0·4189 (1)	0·3127 (2)	−0·04333 (8)	471 (4)
C(18)	0·3607 (2)	0·3527 (4)	0·0179 (1)	500 (6)
N(19)	0·6828 (2)	0·0918 (3)	0·1390 (1)	481 (5)
S(20)	0·82743 (4)	0·02253 (8)	0·01719 (3)	431 (1)
O(21)	0·8615 (1)	0·0010 (3)	−0·05668 (9)	600 (5)
O(22)	0·8259 (1)	−0·1218 (3)	0·0666 (1)	628 (5)
C(23)	0·9056 (2)	0·1742 (4)	0·0689 (1)	533 (6)
C(24)	0·9242 (3)	0·3280 (5)	0·0239 (2)	816 (10)
O(25)	0·5940 (1)	0·2891 (3)	−0·21593 (9)	603 (5)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·415 (4)	C(9)—C(10)	1·506 (3)
C(1)—C(6)	1·375 (3)	C(10)—C(11)	1·544 (4)
C(1)—C(7)	1·506 (3)	C(10)—N(14)	1·468 (3)
C(2)—C(3)	1·386 (3)	C(11)—C(12)	1·494 (5)
C(2)—O(17)	1·354 (3)	C(12)—C(13)	1·528 (5)
C(3)—C(4)	1·399 (4)	C(13)—N(14)	1·457 (3)
C(4)—C(5)	1·413 (3)	N(14)—C(15)	1·486 (3)
C(4)—N(19)	1·364 (3)	C(15)—C(16)	1·499 (5)
C(5)—C(6)	1·398 (3)	O(17)—C(18)	1·437 (3)
C(5)—S(20)	1·759 (2)	S(20)—O(21)	1·435 (2)
C(7)—O(25)	1·229 (3)	S(20)—O(22)	1·439 (3)
C(7)—N(8)	1·322 (3)	S(20)—C(23)	1·770 (3)
N(8)—C(9)	1·451 (3)	C(23)—C(24)	1·492 (5)

C(2)—C(1)—C(6)	117·4 (2)	C(9)—C(10)—C(11)	114·5 (2)
C(2)—C(1)—C(7)	125·2 (2)	C(9)—C(10)—N(14)	114·6 (2)
C(6)—C(1)—C(7)	117·5 (2)	C(11)—C(10)—N(14)	103·5 (2)
C(1)—C(2)—C(3)	120·6 (2)	C(10)—C(11)—C(12)	105·8 (3)
C(1)—C(2)—O(17)	116·6 (2)	C(11)—C(12)—C(13)	105·8 (3)
C(3)—C(2)—O(17)	122·9 (2)	C(12)—C(13)—N(14)	103·2 (2)
C(2)—C(3)—C(4)	121·9 (2)	C(10)—N(14)—C(13)	105·8 (2)
C(3)—C(4)—C(5)	117·4 (2)	C(10)—N(14)—C(15)	110·8 (2)
C(3)—C(4)—N(19)	119·5 (3)	C(13)—N(14)—C(15)	112·0 (2)
C(5)—C(4)—N(19)	123·2 (2)	N(14)—C(15)—C(16)	112·9 (2)
C(4)—C(5)—C(6)	120·0 (2)	C(2)—O(17)—C(18)	118·9 (2)
C(4)—C(5)—S(20)	121·5 (2)	C(5)—S(20)—C(23)	106·4 (1)
C(6)—C(5)—S(20)	118·6 (2)	C(5)—S(20)—O(21)	108·1 (2)
C(1)—C(6)—C(5)	122·7 (2)	O(21)—S(20)—O(22)	118·6 (1)
C(1)—C(7)—N(8)	118·2 (2)	O(21)—S(20)—C(23)	108·3 (1)
C(1)—C(7)—O(25)	120·4 (2)	C(5)—S(20)—O(22)	108·4 (1)
N(8)—C(7)—O(25)	121·4 (2)	O(22)—S(20)—C(23)	106·5 (1)
C(7)—N(8)—C(9)	122·7 (2)	S(20)—C(23)—C(24)	114·3 (2)
N(8)—C(9)—C(10)	112·1 (2)		

C(2)—C(1)—C(7)—N(8)	−29·0 (4)	C(9)—C(10)—N(14)—C(13)	162·4 (2)
C(2)—C(1)—C(7)—O(25)	153·2 (3)	C(9)—C(10)—C(11)—C(12)	−144·4 (3)
C(1)—C(2)—O(17)—C(18)	−176·2 (2)	C(10)—C(11)—C(12)—C(13)	−4·8 (4)
C(4)—C(5)—S(20)—O(21)	174·8 (2)	C(12)—C(13)—N(14)—C(10)	−40·3 (3)
C(4)—C(5)—S(20)—O(22)	45·1 (3)	C(10)—N(14)—C(15)—C(16)	180·0 (3)
C(4)—C(5)—S(20)—C(23)	−69·2 (3)	C(5)—S(20)—C(23)—C(24)	−69·9 (3)
C(7)—N(8)—C(9)—C(10)	−160·6 (3)	C(1)—C(7)—N(8)—H(8)	0 (2)
N(8)—C(9)—C(10)—C(11)	54·5 (3)	C(3)—C(4)—N(19)—H(19*A*)	1 (2)
N(8)—C(9)—C(10)—N(14)	−64·7 (3)	C(5)—C(4)—N(19)—H(19*B*)	−23 (2)
C(9)—C(10)—N(14)—C(15)	−76·0 (3)		

Co. (1985) *REDU*4 program, Lorentz and polarization corrections, absorption corrections by the method of North, Phillips & Mathews (1968) based on one reflection (033). Scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion corrections were included for all non-H atoms (Ibers & Hamilton, 1964). The structure was solved by *MULTAN*82 (Main *et al.*, 1982). The *E* map calculated from the solution with the best figure of merit showed 22 of the 25 non-hydrogen atoms. The remaining C atoms were located in a subsequent difference map. Refinement on *F* by full-matrix least squares, first with isotropic temperature factors and finally anisotropically. All H atoms were found in a difference synthesis and they were included in the refinement with fixed isotropic temperature factors of their parent atoms. Final $R = 0{\cdot}038$, $wR = 0{\cdot}053$, with $w = [1 + (F_o - A)^2/B^2]^{-1}$, where $A = 8$ and $B = 300$. Largest parameter shift/e.s.d. = 0·10. Min. and max. residual electron density −0·38 and 0·21 e $Å^{-3}$. The number of reflections per refined variable was 2405/308 = 7·8. All calculations were performed on a PDP-11/73 microcomputer using *SDP*/*PDP* (Enraf–Nonius, 1982) and *PARST* (Nardelli, 1983).*

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths, bond angles and selected torsion angles are given in Table 2. An *ORTEP* plot (Johnson, 1976) of the molecule, with the adopted numbering scheme, is shown in Fig. 1.

The molecule adopts a folded conformation described by the *gauche* conformation of the N(8)—C(9)—C(10)—N(14) chain [torsion angle is −64·7 (3)°]; the dihedral angle formed by the weighted least-squares planes through the aromatic and pyrrolidine ring is 91·6 (1)°. Such a conformation is in contrast with the solid-state conformations of many other neuroleptic *o*-methoxybenzamides including sulpiride (Blaton, Peeters & De Ranter, 1981) and eticlopride (Wägner, Stensland, Csöregh & De Paulis, 1985), but quite in agreement with FLA797 (Högberg, Rämsby, De Paulis, Stensland, Csöregh & Wägner, 1986).

The two substituents of the pyrrolidine ring are both placed in a quasiequatorial position with

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52292 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

respect to the ring. Using the method of Cremer & Pople (1975), we calculated a phase angle φ_2 = 101·0 (6)°, halfway between envelope and twist $({}_{4}E/{}_{4}^{3}T)$, and a puckering amplitude q_2 = 0·376 (3) Å for the sequence C(11)—C(12)—C(13)—N(14)—C(10). As this amplitude is close to the 0·38 Å of a normal pyrrolidine ring (Pfafferott, Oberhammer, Boggs & Caminati; 1985), any disorder can be excluded. However, the bond length C(11)—C(12) of 1·494 (5) Å is rather short. Therefore, it seemed appropriate to carry out a detailed analysis of the internal motions within the pyrrolidine ring by means of a mean-square-displacement-amplitude (MSDA) analysis (Rosenfield, Trueblood & Dunitz, 1978). Recalling that the pyrrolidine ring is perpendicular to the benzamide moiety, thereby adopting a *T*-shaped conformation, the motion of the pyrrolidine atoms in the direction perpendicular to their plane can be monitored from any atom in the aromatic ring. As can be seen from Table 3, the differences in MSDA between C(12) and the atoms of the aromatic ring are about five to six times larger than the equivalent differences in MSDA for the other pyrrolidine atoms. The next largest differences in MSDA between a pyrrolidine atom and the aromatic ring atoms are found for C(11), with values about two times larger than for C(10), C(13) and N(14). This means that both atoms [C(11) and C(12)] undergo a thermal motion in the direction perpendicular to the pyrrolidine ring, although much more pronounced for C(12).

This aromatic ring is roughly planar, although the atoms are slightly displaced from the least-squares plane [max. deviation is 0·021 (2) Å for C(3)]. In order to compare the bond angles C(2)—C(1)—C(7), C(1)—C(2)—O(17), C(2)—C(1)—C(6) and C(3)—C(4)—C(5) with those of similar compounds, the Cambridge Structural Database (CSD) (Allen *et al.*, 1979) was searched for the 4-amino-2-methoxybenzamide fragment, and five structures (hereafter abbreviated as the 'CSD compounds') were retrieved (identified by CSD reference code): (1) AMBZCL (Blaton, Peeters, De Ranter, Denisoff & Molle, 1980), (2) DEFYIW (Furuya, Iwanami, Takenaka & Sasada, 1985), (3) DUXPIV (Furuya, Iwanami, Takenaka & Sasada, 1986), (4) DUZRAR (Furuya, Fujita, Iwanami, Takenaka & Sasada, 1986) and (5) METPRA01 (Shin, Chang & Koo, 1983). As expected, the bond angles of the title compound do not differ significantly from the CSD means, which are C(2)—C(1)—C(6) = 116·7 (7), C(3)—C(4)—C(5) = 117·2 (3), C(2)—C(1)—C(7) = 127·0 (8) and C(1)—C(2)—O(17) = 116·9 (8)°. No individual angle deviates more than 2σ from the mean. From this it is reasonable to assume that the 4-amino-2-methoxybenzamide moiety adopts a quinonoidal form (Furuya, Iwanami, Takenaka & Sasada, 1982), which is reflected by (1) the C(2)—C(1)—C(6) and C(3)—C(4)—C(5) bond angles which are smaller than the values for $\alpha(CONH_2)$ and $\alpha(NH_2)$ reported by Di Rienzo, Domenicano & Foresti Serantoni (1977) and Domenicano & Murray-Rust (1979): 119·4 (2) and 118·8 (2)° respectively (α is the C—C—C angle at the *ipso* atom in benzamide and aniline derivatives); (2) the nearly sp^2 hybridization state of N(19) [the sum of the valence angles around N(19) is 356 (4)° for the title compound and 356 (6)° (averaged) for the CSD compounds]; and (3) the shortened C(4)—N(19) bond length. However, the endocyclic C(2)—C(3), C(5)—C(6) and the exocyclic C(1)—C(7) bond distances do not show any shortening which could be expected for a quinoidal form [for tables of bond lengths determined by X-ray diffraction see Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987)].

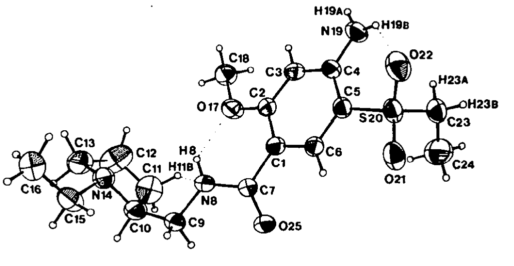

Fig. 1. An *ORTEP* plot (Johnson, 1976) showing 50% probability vibrational ellipsoids for the non-H atoms. Dashed lines indicate intramolecular hydrogen bonds.

Table 3. *Absolute differences in mean square displacement amplitudes* ($Å^2 \times 10^4$) *for selected atom pairs*

	C(10)	C(11)	C(12)	C(13)	N(14)
C(1)	15·5	18·7	106·3	9·7	0·4
C(2)	10·0	31·7	129·2	18·8	5·0
C(3)	20·6	18·6	115·8	4·4	9·4
C(4)	12·6	28·9	127·0	11·9	1·9
C(5)	12·8	27·4	124·0	10·6	3·5
C(6)	19·5	13·6	106·0	3·2	7·2

Table 4. *Geometry of possible hydrogen bonds* [H-*atom positions normalized to* C—H = 1·09 *and* N—H = 1·00 Å (*Allen et al.*, 1987)] *with e.s.d.'s in parentheses*

	$d(H\cdots Y)$ (Å)	$d(X\cdots Y)$ (Å)	$X—H\cdots Y$ (°)
N(8)—H(8)···O(17)	2·06 (3)	2·723 (3)	122 (2)
N(19)—H(19*B*)···O(22)	2·22 (3)	2·954 (3)	129 (2)
C(11)—H(11*B*)···N(8)	2·47 (3)	2·970 (3)	107 (2)
C(23)—H(23*B*)···O(21^{i})	2·48 (3)	3·432 (3)	146 (2)
N(19)—H(19*A*)···O(25^{ii})	2·14 (3)	3·084 (3)	156 (3)
N(19)—H(19*B*)···N(14^{iii})	2·47 (3)	3·228 (3)	132 (2)

Symmetry codes: (i) $2-x, -y, -z$; (ii) $x, 0·5-y, 0·5+z$; (iii) $1-x, -y, -z$.

Because the C(2)—O(17) bond length is relatively short, there must exist some π conjugation between O(17) and the aromatic ring, forcing C(18) to lie in the plane [deviation from the least-squares plane is 0·095 (3) Å]. Owing to the large steric repulsion between the methoxy group and H(3), the C(3)—C(2)—O(17) angle has increased and the C(1)—C(2)—O(17) angle has decreased.

The intra- and intermolecular hydrogen bonds which determine the conformation of the molecule are summarized in Table 4. Two intramolecular hydrogen bonds each form an additional six-membered pseudoring which is fused with the aromatic ring. The strongest of these hydrogen bonds [a nearest-neighbour contact of $d = 0{\cdot}64$ Å, with d defined as being the sum of the van der Waals radii of H and the acceptor atom minus the interatomic distance between both atoms (Taylor & Kennard, 1982)] is typical of most of the solid-state structures of 2-methoxybenzamides and links H(8) with O(17), while the other can be located between H(19*B*) and O(22) ($d = 0{\cdot}48$ Å).

The plane through the amide moiety forms a dihedral angle of 27·9 (1)° with the plane of the aromatic ring, as opposed to many other 2-methoxybenzamides where the dihedral angle is nearly zero (*e.g.* Blaton *et al.*, 1981; Furuya *et al.*, 1982). This deviation is probably due to the intermolecular hydrogen bond between O(25) and H(19*A*)—N(19), causing O(25) [and therefore also N(8)] to deviate from the aromatic plane. A second intermolecular hydrogen bond is found between C(23)—H(23*B*) and O(21), and is compatible with the description of Taylor & Kennard (1982), having $d = 0{\cdot}22$ Å, and the immediate adjacency of a positively charged sulfoxy group to the proton donor. The hydrogen bonds are illustrated in Fig. 2.

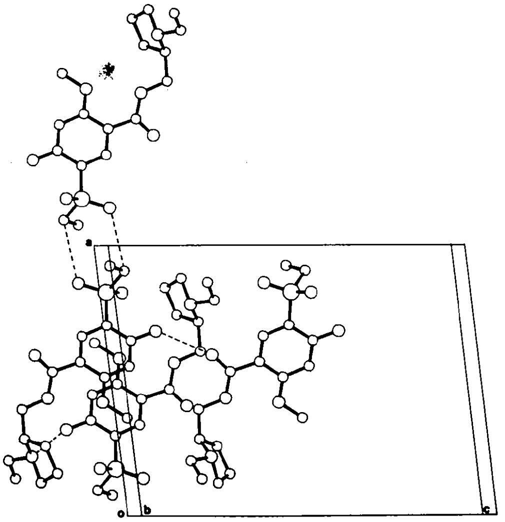

Fig. 2. A *PLUTO* plot (Motherwell & Clegg, 1978) showing the various intermolecular hydrogen bonds in the crystal structure as indicated by dashed lines.

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$Na_2W_2O_7$ (II), A High-Pressure Phase of Disodium Ditungstate(VI)

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Abstract. $Na_2W_2O_7$ (II), $M_r = 525{\cdot}68$, orthorhombic, $Cmc2_1$, $a = 3{\cdot}7777\,(7)$, $b = 26{\cdot}6067\,(38)$, $c = 5{\cdot}4290\,(7)$ Å, $V = 545{\cdot}68$ Å^3, $Z = 4$, $D_x = 6{\cdot}40$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 44{\cdot}654$ mm^{-1}, $F(000) = 855{\cdot}93$. The structure was refined to $R = 0{\cdot}038$, $wR = 0{\cdot}025$ for 1338 absorption-corrected observed reflections. $Na_2W_2O_7$ (II) has been synthesized from the normal-pressure phase at a hydrostatic pressure of 3·2 GPa and $T = 1475$ K. The structure comprises distorted perovskite-type slabs which are composed of WO_6 octahedra [W(1)—O 1·73–2·13, W(2)—O 1·72–2·29 Å] and Na atoms [Na(1)—O 2·46–2·95 Å]. Na(2) is situated between the slabs and has a sevenfold coordination by oxygen [Na(2)—O 2·39–2·89 Å].

Experimental. Experiments were carried out in a modified Belt-type high-pressure apparatus (Range & Leeb, 1975) using gold as the crucible material and starting with the normal-pressure modification $Na_2W_2O_7$ (I) (Okada, Morikawa, Marumo & Iwai, 1975). After quenching from 3·2 GPa and 1475 K a new phase was obtained and proved to be homogenous by Guinier photographs. Heating of this phase at ambient pressure and 1050 K results in complete retransformation to $Na_2W_2O_7$ (I). Therefore, the new phase [NaW_2O_7 (II)] is a high-pressure phase, metastable at normal conditions.

Single crystals, suitable for a crystal structure determination, could be isolated after very slow cooling from 1475 K at 3·2 GPa. A light-bluish crystal fragment (approx. 30 × 30 × 90 μm) was used for data collection on an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, graphite monochromator, $T = 296$ K). Lattice parameters were refined from 2θ values of 25 reflections in the range 4·8–16·4°. Intensities measured for $2 \le \theta \le 35°$; ω–2θ-scan technique [scan width $(1{\cdot}00 + 0{\cdot}34\tan\theta)°$]. Three standard reflections indicated no loss of intensity during data collection. Merging of the 4661 collected intensities ($\sin\theta_{\max}/\lambda = 0{\cdot}807$ Å^{-1}; $-6 \le h \le +6$, $-21 \le k \le +18$, $-8 \le l \le +8$) gave 1338 unique reflections ($R_{\rm int} = 0{\cdot}030$) with $F > 1\sigma(F)$, which were considered as observed and used for all calculations (program system *SHELX76*; Sheldrick, 1976).

From the systematic absences for hkl ($h + k$ odd) and $h0l$ (l odd) the diffraction symbol $C{*}c{*}$ was derived, giving the possible space groups $C2cm$, $Cmc2_1$ and $Cmcm$. Statistics of the normalized E values suggested a non-centrosymmetric space group. This was confirmed by the results of the structure refinement which showed space group $Cmc2_1$ to be the correct one.

The W atom positions were derived from a Patterson map, the remaining atoms were found in successive difference Fourier maps. In least-squares refinement $|F|$ magnitudes were used to refine atomic coordinates and isotropic temperature factors. Convergence was obtained after a few cycles at $R = 0{\cdot}041$. At this stage a numerical correction for absorption (program *DIFABS*; Walker & Stuart, 1983) (max. and min. values 0·94 and 1·14) was

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