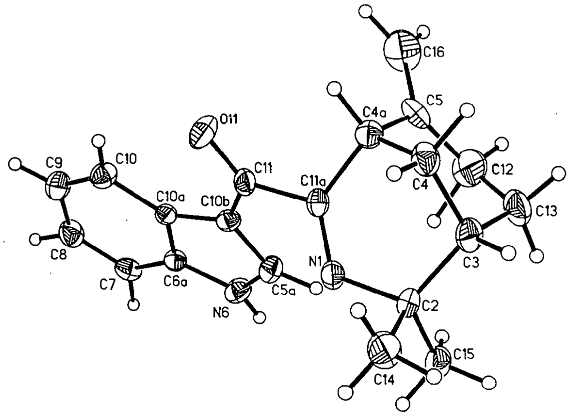

Fig. 1. Drawing of compound (1) with thermal ellipsoids at the 25% probability level. H atoms are represented by spheres of arbitrary size.

Table 2 interatomic distances and valence angles.* Fig. 1 is a thermal-ellipsoid drawing of (1).

Discussion. The indole portion of the molecule is planar (0·018 Å r.m.s.d.), and the N atom exhibits sp^2 hybridization. There is considerable delocalization in the five-membered ring with the C(5*a*)—C(10*b*) double bond elongated to 1·377 (7) Å, the two N(6)—C(sp^2) bonds of 1·344 (7) and 1·383 (6) Å and C(10*a*)—C(10*b*) = 1·444(6) Å. The carbonyl group is almost coplanar with the indole moiety with C(11)—C(10*b*) = 1·449 (6) Å but not with the π system of the heterocyclic ring which is twisted 47·4 (7)° out of the plane resulting in C(11)—C(11*a*) = 1·515 (7) Å. The C(5*a*)—C(10*b*) bond is equivalent to the average value of the distances around the phenyl ring. The cyclohexane ring is in a slightly flattened chair conformation due to the C(5)—C(16) double bond. *cis* fusion and a double bond lead to a 1,2-diplanar conformation for the heterocyclic six-membered ring. The bond lengths and angles in this portion of the molecule are normal. There are only two intermolecular contacts less than 2·5 Å.

We thank the Welch Foundation (P-074), the TCU Research Foundation, Fondo Nacional de Ciencias (Chile) and the Organization of American States for their financial support.

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51872 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of (20*R*)-20,21-Epoxy-19-norpregna-1,3,5(10)-triene-3,17β-diol

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Abstract. $C_{20}H_{26}O_3$, $M_r = 314{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}25\ (1)$, $b = 25{\cdot}36\ (2)$, $c = 13{\cdot}11\ (1)$ Å, $V = 3410{\cdot}14$ Å^3, $Z = 8$, $D_x = 1{\cdot}225$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}45$ cm^{-1}, $F(000) = 1352$, $T = 293$ K. The structure was solved by direct methods and refined to $R = 0{\cdot}051$ for 2384 reflections with $F/\sigma(F) > 5$. Both the crystallographically independent molecules are in one 20*R* configuration

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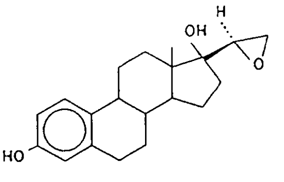
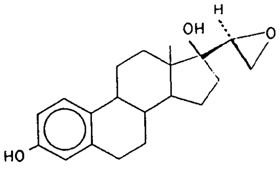
and confirm predictions based on mechanistic and stereochemical arguments. In the crystal lattice the molecules form a two-dimensional network of hydrogen bonds approximately perpendicular to **c**.

Introduction. As part of a project to investigate compounds selectively toxic to oestrogen-dependent tumours, the title compound (1) and its 20*S* isomer (2) were prepared by Gill, Lockey, Marples & Traynor (1986).



(1)



(2)

It was believed that the steroids may have alkylating properties whilst still retaining their hormonal properties. The epoxide group was chosen as the alkylator as it is relatively small and therefore may disturb receptor binding less than larger groups. It has also relatively low activity, reducing the potential for nonselective alkylation on passage to the target cell. The epoxides (1) and (2) were tested for cytotoxicity against HeLaS3 cells (human cervical cancer) and GH3 cells (rat pituitary adenoma). Both isomers were toxic to either cell line but one was more active than the other and showed more efficient oestrogen-receptor binding. Stereochemical arguments indicate that the 20*R* diastereoisomer is the more active form (Gill *et al.*, 1986) and to confirm this an X-ray crystal-structure determination has been undertaken.

Experimental. Preparation by the method of Gill *et al.* (1986); colourless acicular crystal 1·3 × 0·3 × 0·2 mm mounted about **a**, Stoe Stadi-2 Weissenberg diffractometer, $(\sin\theta)/\lambda < 0{\cdot}6$ Å^{-1}; lattice parameters from optimum fit of axial row reflections ($10 < 2\theta < 25°$); 3582 unique reflections measured of which 2384 had $F/\sigma(F) > 5$ and were classed as observed; h $0\rightarrow 10$, k $0\rightarrow 30$, l $0\rightarrow 15$; standard reflection on each layer measured for every 50 reflections, no significant change; no correction for absorption or extinction; structure solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and refined by full-matrix least squares based on F to $R = 0{\cdot}051$, $wR = 0{\cdot}054$, all non-H atoms anisotropic, H atoms found from difference map and not refined; on the final refinement cycle (415 parameters) $w = 1{\cdot}2930/[\sigma^2(F) + 0{\cdot}001339F^2]$; max. $\Delta/\sigma = 0{\cdot}36$, $\Delta\rho$ excursions $\pm 0{\cdot}2$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974); structure refinement using *SHELX*76 (Sheldrick, 1976) and geometry calculations using *XTAL*83 (Stewart & Hall, 1983) as implemented at Loughborough University Computer Centre and University of Manchester Regional Computer Centre respectively.

Table 1. *Final positional parameters* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = (8\pi^2/3)(\sum U_{ii})$.

	x	y	z	B_{eq}
C(11)	−969 (4)	720 (1)	−111(3)	3·3 (2)
C(12)	−712 (4)	1247 (1)	102 (4)	3·6 (3)
C(13)	−694 (4)	1415 (1)	1099 (4)	3·4 (3)
C(14)	−908 (4)	1059 (2)	1869 (3)	3·8 (3)
C(15)	−1168 (4)	528 (1)	1664 (3)	3·2 (2)
C(16)	−1407 (5)	165 (2)	2565 (4)	4·3 (3)
C(17)	−2073 (5)	−351 (1)	2243 (3)	3·7 (3)
C(18)	−1338 (4)	−579 (1)	1342 (3)	2·9 (2)
C(19)	−1502 (4)	−223 (1)	404 (3)	2·9 (2)
C(110)	−1174 (4)	354 (1)	657 (3)	2·8 (2)
C(111)	−747 (4)	−432 (1)	−517 (3)	3·5 (2)
C(112)	−1039 (4)	−1017 (2)	−756 (3)	3·6 (3)
C(113)	−842 (4)	−1358 (1)	199 (3)	2·8 (2)
C(114)	−1721 (4)	−1137 (1)	1054 (3)	2·8 (2)
C(115)	−1727 (4)	−1572 (2)	1877 (3)	3·8 (3)
C(116)	−1572 (4)	−2094 (2)	1258 (4)	3·8 (3)
C(117)	−1313 (4)	−1938 (3)	128 (3)	3·1 (2)
C(118)	595 (4)	−1363 (2)	507 (4)	4·0 (3)
C(120)	−2586 (4)	−1985 (1)	−450 (4)	3·7 (3)
C(121)	−2683 (5)	−2182 (2)	−1505 (4)	5·1 (3)
O(13)	−467 (3)	1933 (1)	1353 (3)	4·7 (2)
O(117)	−411 (3)	−2287 (1)	−347 (2)	3·8 (2)
O(120)	−3022 (3)	−2518 (1)	−643 (3)	4·7 (2)
C(21)	−4275 (5)	−5533 (2)	−7126 (4)	3·7 (3)
C(22)	−4542 (5)	−6059 (2)	−7317 (4)	4·2 (3)
C(23)	−4477 (4)	−6418 (1)	−6528 (4)	3·5 (3)
C(24)	−4113 (4)	−6252 (2)	−5570 (4)	3·5 (3)
C(25)	−3832 (4)	−5723 (2)	−5381 (3)	3·2 (2)
C(26)	−3479 (5)	−5564 (2)	−4291 (4)	4·2 (3)
C(27)	−3045 (5)	−4992 (2)	−4180 (4)	3·9 (3)
C(28)	−3877 (4)	−4630 (1)	−4850 (3)	3·0 (2)
C(29)	−3619 (4)	−4768 (2)	−5974 (3)	3·1 (2)
C(210)	−3929 (4)	−5350 (1)	−6164 (3)	3·0 (2)
C(211)	−4325 (6)	−4396 (2)	−6712 (4)	4·5 (3)
C(212)	−4070 (6)	−3807 (2)	−6475 (4)	4·3 (3)
C(213)	−4387 (4)	−3679 (1)	−5370 (3)	3·0 (2)
C(214)	−3569 (4)	−4046 (1)	−4674 (3)	3·0 (2)
C(215)	−3729 (5)	−3815 (2)	−3608 (4)	4·0 (3)
C(216)	−3785 (5)	−3211 (2)	−3784 (4)	4·5 (3)
C(217)	−3970 (4)	−3124 (1)	−4958 (5)	3·4 (3)
C(218)	−5854 (4)	−3738 (2)	−5166 (4)	4.5 (3)
C(220)	−2718 (4)	−2946 (2)	−5457 (4)	3·8 (3)
C(221)	−2689 (5)	−2595 (2)	−6338 (5)	5·4 (4)
O(23)	−4780 (4)	−6931 (1)	−6761 (3)	5·3 (2)
O(217)	−4855 (3)	−2706 (1)	−5166 (3)	4·4 (2)
O(220)	−2423 (3)	−2386 (1)	−5315 (3)	4·8 (2)

Discussion. The final atomic coordinates are listed in Table 1.* Bond lengths, angles and principal intermolecular contacts are listed in Table 2.

One of the two crystallographically independent molecules with atom numbering is shown in Fig. 1. The structure analysis confirms the *R* configuration at C(20) and is in agreement with that predicted from mechanistic and stereochemical arguments (Gill *et al.*, 1986). Although the two enantiomorphs gave identical *R* factors, the absolute configuration was

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51843 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

apparent from the known configuration of the steroid nucleus.

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

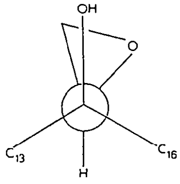
Molecule *A*		Molecule *B*	
C(11)—C(12)	1·391 (4)	C(21)—C(22)	1·385 (7)
C(11)—C(110)	1·386 (5)	C(21)—C(210)	1·390 (7)
C(12)—C(13)	1·375 (7)	C(22)—C(23)	1·380 (7)
C(13)—C(14)	1·372 (6)	C(23)—C(24)	1·376 (7)
C(13)—O(13)	1·375 (7)	C(23)—O(23)	1·372 (4)
C(14]—C(15)	1·399 (6)	C(24)—C(25)	1·395 (7)
C(15)—C(16)	1·518 (6)	C(25)—C(26)	1·528 (7)
C(15)—C(110)	1·392 (5)	C(25)—C(210)	1·400 (6)
C(16)—C(17)	1·535 (6)	C(26)—C(27)	1·525 (7)
C(17)—C(18)	1·516 (6)	C(27)—C(28)	1·531 (6)
C(18)—C(19)	1·535 (5)	C(28)—C(29)	1·538 (6)
C(18)—C(14)	1·517 (4)	C(28)—C(214)	1·532 (4)
C(19)—C(110)	1·538 (4)	C(29)—C(210)	1·530 (6)
C(19)—C(111)	1·529 (5)	C(29)—C(211)	1·533 (7)
C(111)—C(112)	1·546 (6)	C(211)—C(212)	1·548 (7)
C(112)—C(113)	1·535 (6)	C(212)—C(213)	1·520 (7)
C(113)—C(114)	1·544 (5)	C(213)—C(214)	1·550 (5)
C(113)—C(117)	1·551 (4)	C(213)—C(217)	1·567 (4)
C(113)—C(118)	1·528 (6)	C(213)—C(218)	1·535 (6)
C(114)—C(115)	1·543 (6)	C(214)—C(215)	1·524 (6)
C(115)—C(116)	1·561 (7)	C(215)—C(216)	1·550 (7)
C(116)—C(117)	1·556 (7)	C(216)—C(217)	1·567 (7)
C(117)—C(120)	1·514 (6)	C(217)—C(220)	1·510 (6)
C(117)—O(117)	1·424 (5)	C(217)—O(217)	1·422 (4)
C(120)—C(121)	1·474 (7)	C(220)—C(221)	1·459 (8)
C(120)—O(120)	1·446 (4)	C(220)—O(220)	1·464 (6)
C(121)—O(120)	1·458 (6)	C(221)—O(220)	1·468 (7)
C(12)—C(11)—C(110)	121·8 (4)	C(22)—C(21)—C(210)	122·4 (4)
C(11)—C(12)—C(13)	119·4 (4)	C(21)—C(22)—C(23)	119·4 (5)
C(12)—C(13)—C(14)	119·6 (3)	C(22)—C(23)—C(24)	119·7 (4)
C(12)—C(13)—O(13)	121·9 (4)	C(22)—C(23)—O(23)	116·6 (5)
C(14)—C(13)—O(13)	118·5 (4)	C(24)—C(23)—O(23)	123·7 (4)
C(13)—C(14)—C(15)	121·5 (4)	C(23)—C(24)—C(25)	120·8 (4)
C(14)—C(15)—C(16)	117·7 (4)	C(24)—C(25)—C(26)	118·0 (4)
C(14)—C(15)—C(110)	119·2 (3)	C(24)—C(25)—C(210)	120·4 (4)
C(16)—C(15)—C(110)	123·0 (3)	C(26)—C(25)—C(210)	121·6 (4)
C(15)—C(16)—C(17)	112·0 (4)	C(25)—C(26)—C(27)	114·2 (4)
C(16)—C(17)—C(18)	108·6 (4)	C(26)—C(27)—C(28)	110·7 (4)
C(17)—C(18)—C(19)	110·2 (3)	C(27)—C(28)—C(29)	108·5 (3)
C(17)—C(18)—C(114)	114·9 (3)	C(27—C(28)—C(214)	112·3 (3)
C(19)—C(18)—C(114)	108·7 (3)	C(29)—C(28)—C(214)	109·2 (3)
C(18)—C(19)—C(110)	111·3 (3)	C(28)—C(29)—C(210)	109·9 (3)
C(18)—C(19)—C(111)	111·9 (3)	C(28)—C(29)—C(211)	112·6 (4)
C(11)—C(110)—C(15)	118·4 (3)	C(21)—C(210)—C(25)	117·3 (3)
C(11)—C(110)—C(19)	120·9 (3)	C(21)—C(210)—C(29)	121·5 (4)
C(15)—C(110)—C(19)	120·5 (3)	C(25)—C(210)—C(29)	121·2 (4)
C(19)—C(111)—C(112)	113·3 (3)	C(29)—C(211)—C(212)	112·8 (4)
C(111)—C(112)—C(113)	110·5 (3)	C(211)—C(212)—C(213)	111·2 (4)
C(112)—C(113)—C(114)	108·1 (3)	C(212)—C(213)—C(214)	108·5 (3)
C(112)—C(113)—C(117)	116·4 (3)	C(212)—C(213)—C(217)	117·5 (4)
C(112)—C(113)—C(118)	110·3 (3)	C(212)—C(213)—C(218)	110·8 (4)
C(114)—C(113)—C(117)	101·9 (3)	C(214)—C(213)—C(217)	100·9 (3)
C(117)—C(113)—C(118)	108·0 (3)	C(217)—C(213)—C(218)	107·2 (3)
C(18)—C(114)—C(113)	111·6 (3)	C(28)—C(214)—C(213)	112·4 (3)
C(18)—C(114)—C(115)	119·6 (3)	C(28)—C(214)—C(215)	119·2 (3)
C(113)—C(114)—C(115)	104·5 (3)	C(213)—C(214)—C(215)	104·5 (3)
C(114)—C(115)—C(116)	104·0 (3)	C(214)—C(215)—C(216)	104·3 (4)
C(15)—C(116)—C(117)	107·3 (4)	C(215)—C(216)—C(217)	106·9 (4)
C(113)—C(117)—C(116)	103·7 (3)	C(213)—C(217)—C(216)	104·2 (3)
C(113)—C(117)—C(120)	111·9 (3)	C(213)—C(217)—C(220)	110·6 (4)
C(113)—C(117)—O(117	114·4 (3)	C(213)—C(217)—O(217)	115·4 (3)
C(116)—C(117)—C(120)	108·0 (3)	C(216)—C(217)—C(220)	111·4 (4)
C(116)—C(117)—O(117)	111·7 (3)	C(216)—C(217)—O(217)	111·8 (4)
C(120)—C(117)—O(117)	107·0 (3)	C(220)—C(217)—O(217)	103·7 (3)
C(117)—C(120)—C(121)	123·7 (4)	C(217)—C(220)—C(221)	122·9 (4)
C(117)—C(120)—O(120)	115·3 (3)	C(217)—C(220)—O(220)	114·2 (4)
C(212)—C(120)—O(120)	59·9 (3)	C(221)—C(220)—O(220)	60·3 (3)
C(120)—C(121)—O(120)	59·1 (3)	C(220)—C(221)—O(220)	60·0 (3)
C(120)—O(120)—C(121)	61·0 (3)	C(220)—O(220)—C(221)	59·7 (3)

Oxygen–oxygen contact distances

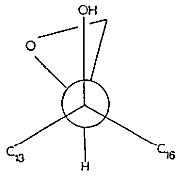
O(13)	O(217)	2·814 (5^{ii})	O(220)	3·284 (5^{ii})	
O(23)	O(117)	2·722 (4^{ii})	O(120)	3·515 (5^{ii})	
O(117)	O(23)	2·722 (4^{ii})	O(120)	2·816 (4^{iii})	2·768 (4^{i})
O(217)	O(13)	2·814 (5^{ii})	O(220)	2·718 (4^{iii})	2·630 (4^{i})
O(120)	O(23)	3·515 (5^{ii})	O(117)	2·816 (4^{iii})	2·768 (4^{i})
O(220)	O(13)	3·284 (5^{ii})	O(217)	2·718 (4^{iii})	2·630 (4^{i})

Symmetry operation: (i) x, y, z; (ii) $0{\cdot}5 - x, -y, 0{\cdot}5 + z$; (iii) $0{\cdot}5 + x, 0{\cdot}5 - y, -z$.

The dihedral angles between the C(20)—O(20) and C(17)—(17) bonds are 47·7 (5) and 41·4 (5)° for the two independent molecules respectively. Although rotation about the C(17)—C(20) bond may be expected in solution and would be necessary for the Payne rearrangement (Payne, 1962), the observed solid-state conformation approximately represented by (3) is sensible in that the epoxyethano group would suffer no significant steric interactions. A similar conformation (4) would be expected for the 20*S* isomer. The previously observed greater oestrogen-binding efficiency of the 20*R*-3,17-dihydroxy-20,21-epoxide (1) *versus* its 20*S* isomer is not surprising given that the conformations (3) and (4) are meaningful and that the receptor approach to the 17*β*-OH group is believed to be from the direction opposite the 13*β*-methyl group (Kaspar & Witzel, 1985).



(3)



(4)

There are minor conformational differences between the two crystallographically independent molecules other than that previously discussed, principally the C(2)—C(3)—O(3) and C(4)—C(3)—O(3) angles. These presumably result from the fact that the terminal phenolic O—H bond points in opposite directions in the two molecules. Generally, bond lengths and angles follow expected values, although it should be noted that this is the first reported example of a steroid structure containing an epoxide ring adjacent to a hydroxyl group.

The unit-cell contents, projected down **a** and **c**, are shown in Fig. 2. The molecules are held together in

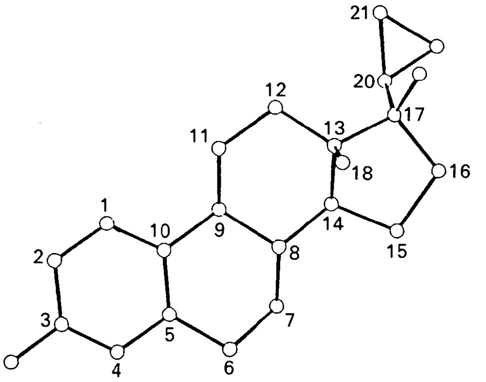


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecular structure and atom numbering.

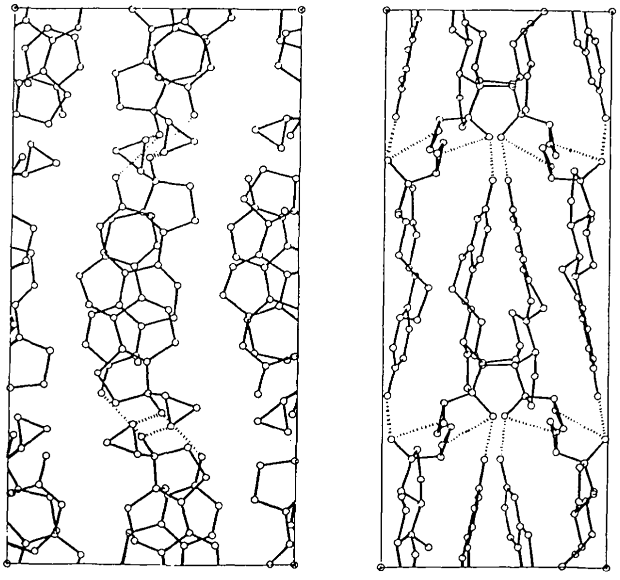

(a) (b)

Fig. 2. Unit-cell contents projected down (a) **a** and (b) **c**.

sheets, approximately perpendicular to **c**, by a network of hydrogen bonds, with principal contacts between O(23)···O(117), O(13)···O(217), O(117)···O(120) and O(217)···O(220). Thus both phenolic hydroxyl groups form hydrogen bonds to an O(17) hydroxyl group in nonequivalent molecules which in turn are intermolecularly hydrogen bonded to epoxide O atoms in equivalent molecules. There is no hydrogen bonding between O(217) and O(120) or O(117) and O(220). As expected there is also no intramolecular hydrogen bonding despite contacts of 2·630 (4) and 2·768 (4) Å respectively, since the geometry is unfavourable and the H atoms involved are pointing towards epoxide O atoms in different molecules.

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Structure Cristalline de la Chloro-4 Bis(chlorométhyl)-3,6 Pyridazine

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Abstract. $C_6H_5Cl_3N_2$, $M_r = 211{\cdot}5$, monoclinic, Cc, $a = 9{\cdot}580(5)$, $b = 12{\cdot}010(6)$, $c = 8{\cdot}413(7)$ Å, $\beta = 119{\cdot}75(6)^\circ$, $V = 840(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}65$ (3), $D_x = 1{\cdot}67$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 10$ cm^{-1}, $F(000) = 424$, $T = 298$ K, $R = 0{\cdot}026$, $wR = 0{\cdot}024$ ($w = 1$) for 1074 independent reflexions. There is no indication that the substitution on C(4) has any significant effect on the bond lengths in the pyridazine moiety, at most the C(4)—C(5) bond is shortened.

Introduction. Nous avons précédemment décrit la synthèse, les études structurales et spectroscopiques de pyridazines bis(hydroxyméthyl) en positions 3,6 (Abraham, Mernari, Lagrenée & Sueur, 1988). Leurs dérivés dicarbaldéhyde-dioxime ainsi que les dérivés dicarboxyliques (Sueur, Lagrenée, Abraham & Brémard, 1987) sont des ligands permettant la formation de complexes binucléaires symétriques dont les atomes métalliques présentent un fort couplage antiferromagnétique (Abraham, Brémard, Lagrenée, Mernari & Sueur, 1986).

Nous envisageons maintenant la synthèse de complexes binucléaires à partir de pyridazines chélatantes dissymétriques substitutées en position 4 par un atome de chlore.

L'obtention de la chloro-4 bis(chlorométhyl)-3,6 pyridazine constitue une étape intermédiaire dans la

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