Table 3. *Geometry of the hydrogen bonds* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(4)—H(4)···O(1W^{i})	0·93 (2)	1·88 (3)	2·761 (3)	158 (2)
O(1*W*)—H(1*W*1)···O(3W^{i})	0·93 (3)	1·87 (3)	2·800 (3)	175 (3)
O(1*W*)—H(2*W*1)···O(46^{ii})	0·91 (3)	1·87 (3)	2·768 (3)	169 (2)
O(2*W*)—H(1*W*2)···Cl(1^{iii})	0·89 (4)	2·27 (4)	3·163 (3)	174 (4)
O(2*W*)—H(2*W*2)···Cl(1^{iv})	0·99 (4)	2·33 (4)	3·318 (3)	174 (4)
O(3*W*)—H(1*W*3)···O(2W^{v})	0·96 (4)	1·88 (4)	2·798 (4)	159 (3)
O(3*W*)—H(2*W*3)···Cl(1^{iii})	0·94 (4)	2·22 (4)	3·141 (3)	170 (4)

Symmetry code (i) x, $0·5-y$, $z-0·5$; (ii) $-x$, $1-y$, $-z$; (iii) x, $0·5-y$, $0·5+z$; (iv) $1-x$, $y-0·5$, $0·5-z$; (v) $x-1$, y, z.

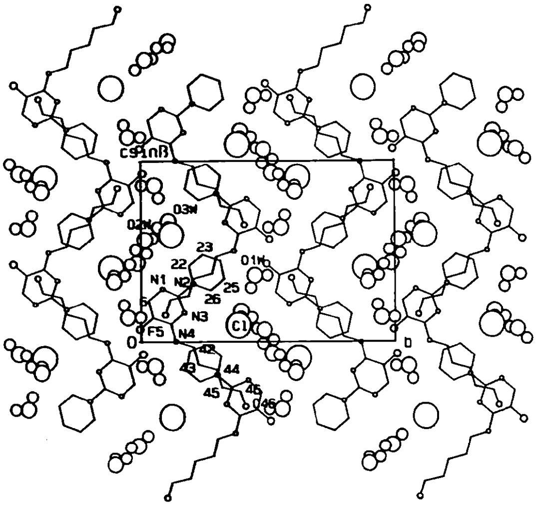

Fig. 2. Crystal packing viewed along **a**. The water molecules are represented as van der Waals space-filling models, and the Cl^- ions as spheres.

the F substituents from two inversion-related cations form a close contact of 2·923 (2) Å (Fig. 2).

Thanks are due to Dr Ryszard Adamiak for his interest and helpful discussions.

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Structure of (−)-Narcotine Hemiacetal

By P. Dokurno

Institute of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 *Gdańsk, Poland*

and M. Jaskólski, Z. Kosturkiewicz,* D. Matecka and M. D. Rozwadowska

Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 *Poznań, Poland*

(*Received* 11 *May* 1990; *accepted* 28 *August* 1990)

Abstract. 1,3-Dihydro-6,7-dimethoxy-3-(5,6,7,8-tetrahydro-4-methoxy-6-methyl-1,3-dioxolo[4,5-*g*]-isoquinolin-5-yl)-1-isobenzofuranol, $C_{22}H_{25}NO_7$, $M_r = 415·4$, orthorhombic, $P2_12_12_1$, $a = 12·302$ (2), $b = 8·022$ (1), $c = 20·929$ (3) Å, $V = 2065·4$ (5) Å^3, $Z = 4$, $D_m = 1·29$, $D_x = 1·34$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 7·91$ cm^{-1}, $F(000) = 880$, room temperature, $R = 0·039$ for 1496 observed reflections. The heterocyclic isoquinoline ring exhibits a half-chair conformation and the two five-membered rings

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* To whom correspondence should be addressed.

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

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

	x	y	z	U_{eq}
C(1)	0·7264 (3)	0·2209 (5)	0·1817 (2)	0·050 (1)
N(2)	0·8134 (3)	0·3178 (4)	0·1501 (2)	0·058 (1)
C(23)	0·8176 (4)	0·4887 (5)	0·1747 (3)	0·074 (2)
C(3)	0·8037 (3)	0·3162 (6)	0·0792 (2)	0·067 (2)
C(4)	0·6966 (3)	0·3819 (6)	0·0543 (2)	0·068 (2)
C(10)	0·5997 (3)	0·3161 (5)	0·0922 (2)	0·051 (1)
C(5)	0·4951 (3)	0·3436 (5)	0·0671 (2)	0·060 (1)
C(6)	0·4093 (3)	0·2959 (6)	0·1035 (2)	0·059 (1)
O(11)	0·3004 (2)	0·3040 (5)	0·0887 (1)	0·085 (1)
C(12)	0·2434 (4)	0·2488 (8)	0·1447 (2)	0·087 (2)
O(13)	0·3213 (2)	0·1780 (5)	0·1870 (1)	0·085 (1)
C(7)	0·4216 (3)	0·2210 (5)	0·1627 (2)	0·056 (1)
C(8)	0·5232 (3)	0·1951 (5)	0·1877 (2)	0·051 (1)
O(24)	0·5411 (2)	0·1205 (4)	0·2462 (1)	0·073 (1)
C(25)	0·4756 (5)	0·1676 (8)	0·2975 (2)	0·097 (2)
C(9)	0·6144 (3)	0·2420 (5)	0·1518 (2)	0·047 (1)
C(14)	0·7575 (3)	0·0336 (5)	0·1900 (2)	0·053 (1)
O(15)	0·8495 (2)	0·0210 (4)	0·2326 (1)	0·062 (1)
C(16)	0·9468 (3)	−0·0059 (5)	0·1976 (2)	0·059 (1)
O(26)	1·0030 (2)	0·1457 (4)	0·1883 (2)	0·076 (1)
C(17)	0·9073 (3)	−0·0807 (4)	0·1356 (2)	0·051 (1)
C(18)	0·9642 (3)	−0·1577 (5)	0·0874 (2)	0·055 (1)
O(27)	1·0757 (2)	−0·1792 (4)	0·0897 (2)	0·077 (1)
C(28)	1·1143 (5)	−0·3069 (11)	0·1254 (4)	0·173 (4)
C(19)	0·9067 (3)	−0·2155 (5)	0·0339 (2)	0·058 (1)
O(29)	0·9680 (3)	−0·2947 (4)	−0·0117 (1)	0·081 (1)
C(30)	0·9106 (5)	−0·3678 (8)	−0·0627 (3)	0·101 (2)
C(20)	0·7956 (3)	−0·1910 (5)	0·0294 (2)	0·061 (1)
C(21)	0·7387 (3)	−0·1114 (5)	0·0782 (2)	0·056 (1)
C(22)	0·7957 (3)	−0·0568 (5)	0·1312 (2)	0·050 (1)

exhibit envelope conformations. There is one, rather strong, intramolecular OH···N hydrogen bond with H···N = 1·64 Å, which stabilizes the β-anomer formed during the reduction of (−)-α-narcotine.

Introduction. (−)-Narcotine hemiacetal, which was isolated from the members of the Papaveraceae family (Sariyar & Shamma, 1986), was synthesized from (−)-α-narcotine (Schmidhammer, 1981). We have prepared it from the same base by partial hydride reduction, using three molar equivalents of dibal as the reducing agent. The molecule has three asymmetric centers [C(1), C(14), C(16)], the first two, C(1) and C(14), were known for the initial substance, while the C(16) center is a result of the reduction reaction.

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

C(1)—N(2)	1·478 (5)	C(8)—C(9)	1·402 (5)
C(1)—C(9)	1·522 (5)	O(24)—C(25)	1·396 (6)
C(1)—C(14)	1·561 (6)	C(14)—O(15)	1·444 (4)
N(2)—C(23)	1·465 (5)	C(14)—C(22)	1·504 (5)
N(2)—C(3)	1·489 (5)	O(15)—C(16)	1·420 (4)
C(3)—C(4)	1·512 (6)	C(16)—O(26)	1·413 (5)
C(4)—C(10)	1·524 (5)	C(16)—C(17)	1·511 (5)
C(10)—C(5)	1·408 (5)	C(17)—C(18)	1·374 (5)
C(10)—C(9)	1·394 (5)	C(17)—C(22)	1·390 (5)
C(5)—C(6)	1.358 (5)	C(18)—O(27)	1·383 (5)
C(6)—O(11)	1·376 (5)	C(18)—C(19)	1·403 (6)
C(6)—C(7)	1·385 (6)	O(27)—C(28)	1·355 (9)
O(11)—C(12)	1·436 (6)	C(19)—O(29)	1·373 (5)
C(12)—O(13)	1·423 (6)	C(19)—C(20)	1·383 (6)
O(13)—C(7)	1·379 (5)	O(29)—C(30)	1·407 (6)
C(7)—C(8)	1·371 (5)	C(20)—C(21)	1·393 (6)
C(8)—O(24)	1·380 (5)	C(21)—C(22)	1·383 (6)

C(9)—C(1)—C(14)	112·0 (3)	C(1)—C(9)—C(8)	118·3 (3)
N(2)—C(1)—C(14)	112·3 (3)	C(1)—C(9)—C(10)	122·2 (3)
N(2)—C(1)—C(9)	114·4 (3)	C(1)—C(14)—C(22)	116·7 (3)
C(1)—N(2)—C(3)	112·5 (3)	C(1)—C(14)—O(15)	109·2 (3)
C(1)—N(2)—C(23)	111·1 (3)	O(15)—C(14)—C(22)	103·1 (3)
C(23)—N(2)—C(3)	111·2 (3)	C(14)—O(15)—C(16)	110·7 (3)
N(2)—C(3)—C(4)	114·2 (3)	O(15)—C(16)—C(17)	103·5 (3)
C(3)—C(4)—C(10)	112·5 (3)	O(15)—C(16)—O(26)	110·7 (3)
C(4)—C(10)—C(9)	120·7 (3)	O(26)—C(16)—C(17)	112·4 (3)
C(4)—C(10)—C(5)	117·8 (3)	C(16)—C(17)—C(22)	108·6 (3)
C(5)—C(10)—C(9)	121·3 (3)	C(16)—C(17)—C(18)	130·2 (3)
C(10)—C(5)—C(6)	117·2 (4)	C(18)—C(17)—C(22)	121·1 (4)
C(5)—C(6)—C(7)	122·6 (4)	C(17)—C(18)—C(19)	118·5 (3)
C(5)—C(6)—O(11)	128·2 (4)	C(17)—C(18)—O(27)	122·4 (4)
O(11)—C(6)—C(7)	109·2 (3)	O(27)—C(18)—C(19)	119·1 (3)
C(6)—O(11)—C(12)	106·1 (3)	C(18)—O(27)—C(28)	117·5 (4)
O(11)—C(12)—O(13)	107·5 (3)	C(18)—C(19)—C(20)	120·3 (4)
C(12)—O(13)—C(7)	105·9 (3)	C(18)—C(19)—O(29)	115·5 (3)
C(6)—C(7)—O(13)	109·9 (3)	O(29)—C(19)—C(20)	124·2 (4)
O(13)—C(7)—C(8)	129·6 (4)	C(19)—O(29)—C(30)	116·4 (4)
C(6)—C(7)—C(8)	120·5 (4)	C(19)—C(20)—C(21)	120·8 (4)
C(7)—C(8)—C(9)	118·9 (4)	C(20)—C(21)—C(22)	118·6 (4)
C(7)—C(8)—O(24)	123·4 (3)	C(17)—C(22)—C(21)	120·6 (3)
O(24)—C(8)—C(9)	117·7 (3)	C(14)—C(22)—C(21)	130·6 (3)
C(8)—O(24)—C(25)	118·3 (4)	C(14)—C(22)—C(17)	108·7 (3)
C(10)—C(9)—C(8)	119·4 (3)		

C(1)—N(2)—C(3)—C(4)	57·7 (4)	N(2)—C(1)—C(14)—O(15)	64·3 (4)
N(2)—C(3)—C(4)—C(10)	−43·8 (5)	C(1)—C(14)—O(15)—C(16)	−101·7 (3)
C(3)—C(4)—C(10)—C(9)	15·6 (5)	C(14)—O(15)—C(16)—C(17)	−23·2 (4)
C(4)—C(10)—C(9)—C(1)	−0·7 (5)	O(15)—C(16)—C(17)—C(22)	13·9 (4)
C(10)—C(9)—C(1)—N(2)	13·2 (5)	C(16)—C(17)—C(22)—C(14)	−0·2 (4)
C(9)—C(1)—N(2)—C(3)	−40·6 (4)	C(22)—C(17)—C(16)—O(26)	−105·5 (4)
C(9)—C(1)—N(2)—C(23)	84·9 (4)	C(17)—C(18)—O(27)—C(28)	79·7 (6)
C(1)—C(9)—C(8)—C(7)	176·8 (3)	C(18)—C(19)—O(29)—C(30)	174·1 (4)
C(9)—C(8)—O(24)—C(25)	138·3 (4)	H(1)—C(1)—N(2)—C(3)	−155
C(6)—C(7)—O(13)—C(12)	−7·6 (5)	H(14)—C(14)—C(22)—C(17)	−137
C(7)—O(13)—C(12)—O(11)	11·7 (5)	H(16)—C(16)—C(17)—C(22)	136
O(13)—C(12)—O(11)—C(6)	−11·4 (5)	H(26)—O(26)—C(16)—C(17)	59
C(12)—O(11)—C(6)—C(7)	6·8 (5)		

Experimental. Crystals obtained from methanol, colorless prisms; m.p. = 439–440·5 K, $[\alpha]_D^{20°\mathrm{C}} = -277°$; D_m measured by flotation. Space group from Weissenberg photographs. Crystal 0·15 × 0·3 × 0·4 mm used for intensity measurements on a Syntex $P2_1$ diffractometer in the θ–2θ scan mode. Cell parameters from a least-squares treatment of the setting angles of 15 reflections with $11 \le 2\theta \le 28°$. No absorption or extinction correction. 1615 reflections with $2\theta \le 115°$ measured in the range h 0→13, k 0→8, l 0→22. No significant intensity variation (±2·6%) for two standard reflections (221, 215) recorded every 98 measurements. Peak profile analysis according to Lehmann & Larsen (1974). 1496 observed reflections with $I \geq 2\sigma(I)$. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986). Full-matrix least-squares refinement [function minimized: $\sum w(F_o - F_c)^2$, with $w^{-1} = \sigma^2(F_o) + 0{\cdot}00005F_o^2$] of anisotropic non-H atoms. Methyl H atoms from molecular geometry, treated as rigid groups and refined with isotropic thermal parameters. Remaining H atoms from $\Delta\rho$ map. $R = 0{\cdot}039$, $wR = 0{\cdot}042$, $\Delta/\sigma \le 0{\cdot}25$, $\Delta\rho_{\max} = 0{\cdot}14$, $\Delta\rho_{\min} = -0{\cdot}16$ e Å^{-3}.

Computer programs: *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986) and local programs (Jaskólski, 1982*a*). Scattering factors used were those stored in *SHELX76*. Molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976).

Discussion. Atomic parameters are given in Table 1, and bond lengths and angles in Table 2.[*]

The labeling sequence and a view of the molecule are presented in Fig. 1. The molecule consists of an isoquinoline fragment with a hydrogenated heterocyclic ring condensed with a five-membered dioxole ring and linked with a hemiacetal group derived from the phthalide system. There are three methoxy groups bonded to C(8), C(18) and C(19), one methyl group on N(2), and a hydroxyl group on C(16).

The bond lengths and angles do not deviate significantly from standard values. The aromatic rings are planar and the normals to their planes form an angle of 126·9 (1)°. The hydrogenated heterocyclic isoquinoline ring exhibits a half-chair conformation characterized by the asymmetry parameter $\Delta C_2 = 2{\cdot}83$ (Duax & Norton, 1975), with C(3) below the ring plane (towards the phthalide fragment) and N(2) above the plane. The C(6)—O(11)—C(12)—O(13)—C(7) and C(14)—O(15)—C(16)—C(17)—C(22) rings both exhibit envelope conformations with asymmetry parameters $\Delta C_s = 0{\cdot}43$ and $\Delta C_s = 0{\cdot}60$, respectively, and with C(12) and O(15) out of the ring planes. The methoxy group on C(19) is nearly coplanar with the C(17)–C(22) ring, while that on C(18) is nearly perpendicular to the plane of this ring. The sum of the valence angles around N(2) is 334·8 (9)° showing its sp^3 hybridization. N(2) accepts an intramolecular hydrogen bond from O(26) closing a seven-membered ring. The geometry of the hydrogen bond is O(26)···N(2) = 2·827 (4), O(26)—H(26) = 1·23, H(26)···N(26) = 1·64 Å and O(26)—H(26)···N(2) = 159°. According to its *ΔHA* parameter (Jaskólski, 1982*b*), this hydrogen bond can be considered as rather strong (*ΔHA* = 36). It is responsible for the preferential formation of the *β*-anomer during the hydride reduction process. The C(1) and C(14) asymmetry centers have opposite configurations, in contrast to the alkaloid corytensine (Wu *et al.*, 1988). The new asymmetry center C(16) has the same configuration as the C(1) center and therefore opposite to that at C(14). In all cases, the reduction studied was completely stereoselective and resulted in (−)-narcotine hemiacetal being formed as the only isomer.

Molecular packing in the unit cell is shown in Fig. 2. There are no unusual intermolecular contacts in the structure.

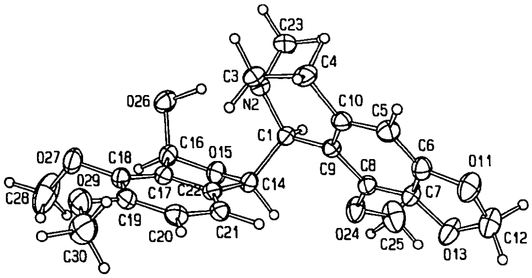

Fig. 1. View of the molecule with the atom-numbering scheme.

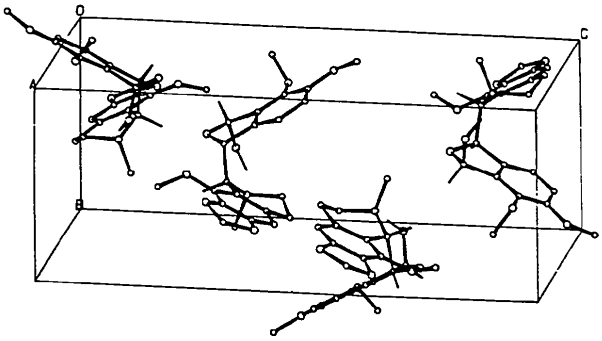

Fig. 2. Packing of the (−)-narcotine hemiacetal molecules in the unit cell.

This work was supported by Project RP.II.10.6.1.5 (MEN).

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53522 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.