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Structure and Stereochemistry of 11-(*o*-Chlorophenyl)-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one Hemiethanol Solvate*

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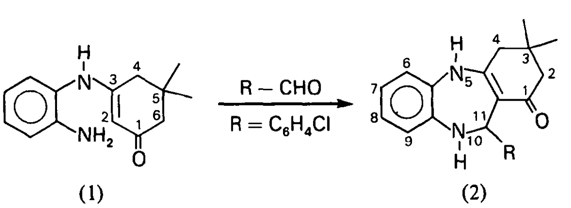
Abstract. $C_{21}H_{21}ClN_2O.\frac{1}{2}C_2H_5OH$, $M_r = 375\cdot9$, monoclinic, $C2/c$, $a = 33\cdot492\,(10)$, $b = 11\cdot045\,(3)$, $c = 28\cdot902\,(9)$ Å, $\beta = 130\cdot68\,(2)°$, $V = 8108\,(1)$ Å^3, $Z = 16$, $D_x = 1\cdot23$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot54178$ Å, $\mu = 1\cdot785$ mm^{-1}, $F(000) = 3184$, $T = 300$ K, $R = 0\cdot072$ for 4100 observed reflections. Two independent molecules in the unit cell. The molecular structure is determined from the X-ray data and confirms the structure previously assigned on the basis of chemical and spectroscopic evidence. In both molecules the seven-membered and cyclohexene rings adopt distorted boat and 1,2-diplanar conformations, respectively, and the benzodiazepine and cyclohexene ring junction is *cis*. The molecules in the crystal are held together by hydrogen bonds.

Introduction. The title compound (2) was prepared by the interaction of an aldehyde with 3-(*o*-aminoanilino)-5,5-dimethyl-2-cyclohexen-1-one (1) and the cyclization is brought about by loss of water (Miyano & Abe, 1972). Compound (2) is useful as a tranquilizer, muscle relaxant and antispasmodic (Abe & Miyano, 1972). The chemical and spectroscopic studies led to the proposal of the chemical structure (2) (Miyano & Abe, 1972; Arellano, Martinez & Cortés, 1982).

The crystal structure of (2) has been determined as part of an investigation of structure–activity relationships for benzodiazepine derivatives.



(1) (2)

Experimental. Colourless crystal 0·28 × 0·36 × 0·37 mm. Nicolet *R*3 four-circle diffractometer. Lattice parameters from 25 machine-centred reflections with $8\cdot1 < 2\theta < 23\cdot6°$. Cu $K\alpha$ radiation. 5099 independent reflections with $3 < 2\theta < 110°$, 4100 with $I > 2\cdot5\sigma(I)$, index range h −34→26, k 0→11, l 0→30, ω-scan mode, variable scan speed, scan width 1·0° (θ), two standard reflections (002, $\bar{1}\bar{1}\bar{1}$) monitored every 50 measurements, Lp correction, absorption ignored. Structure solved by combination of direct methods and partial structure expansion by an iterative *E*–Fourier procedure using *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms treated anisotropically; Cl(*a*), C(20*a*), C(22*a*), C(16*b*), C(2), O(1), C(1) show some disorder [see thermal parameters in Table 1; C(2′) and C(2″) have occupancy factors 0·55 (2) and 0·45 (2) and are treated isotropically]; H atoms in calculated positions riding on the bonded C with fixed isotropic temperature factor, $U = 0\cdot06$ Å^2. H atoms linked to N and O refined. $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + 0\cdot007(F_o)^2]^{-1}$. In the last cycle $(\Delta/\sigma)_{\max} = 0\cdot27$; $\Delta\rho$ from $-0\cdot35$ to $+0\cdot31$ e Å^{-3}, $S = 1\cdot243$. Isotropic extinction parameter $X = 0\cdot00052$. Final $R = 0\cdot072$, $wR = 0\cdot119$. High *R* due to presence of disorder. Scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on a Nova 4S computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs.

Discussion. Atomic coordinates are in Table 1.‡ The bond lengths for non-H atoms are listed in Table 2.

Compound (2) crystallizes with two independent molecules per asymmetric unit. Hereafter, these molecules will be referred to as (2*a*) and (2*b*). Both molecules are closely similar as regards bond lengths and angles. Perspective drawings of the two molecules are shown in Fig. 1.

In both molecules the seven-membered ring has a distorted boat conformation; nevertheless, significant differences in torsion angles of 3–7° occur for the C(12)—C(13) and N(5)—C(14) bonds. Large differences of 11° occur for N(10)—C(11) which defines

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‡ Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, bond angles, selected torsion angles and the results of mean-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43691 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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the orientation of the phenyl ring at C(11) with respect to the benzodiazepine ring system.

The phenyl rings are planar to within the limits of experimental error and show normal geometries, 1·379 Å and 120·0° for the mean $C(sp^2)$—$C(sp^2)$ bond distance and the mean internal angle. This mean bond distance is close to that given by Sutton (1965) [1·395 (5) Å] and Brisse & Sygusch (1974) (1·379 Å). It has been found that interplanar angles between phenyl rings ranging from 54–67° and 77·8–83·7° occur in 5-phenyl and 5-(*o*-chlorophenyl)-1,4-benzodiazepines (Chananont, Hamor & Martin, 1980; Butcher & Hamor, 1985). In this structure the interplanar angles between phenyl rings C(14),C(6), C(7),C(8),C(9),C(15) and C(18)–C(23) are 73·8 (9) and 57·4 (9)° for molecules (2*a*) and (2*b*), respectively.

In (2*a*) and (2*b*), the cyclohexene rings adopt a 1,2-diplanar conformation with C(3*a*) and C(3*b*) 0·31 (1) and 0·32 (1) Å out of the best plane formed by the other five ring atoms and are *cis*-fused to the seven-membered rings.

The extensive system of hydrogen bonds in the crystal structure is illustrated in Fig. 2. There is one intramolecular and three intermolecular bonds; three of them involve the N(5)—H and N(10)—H groups and atoms O(1*a*), O(1) and Cl(1*b*) [N(5*b*)—H(5*b*)···O(1*a*)(−0·5+*x*, 0·5+*y*,*z*); N(10*b*)—H(10*b*)···O(1)-(0·5−*x*, 1·5−*y*, −*z*) and N(10*b*)—H(10*b*)···Cl(1*b*)-(*x*,*y*,*z*)]. In addition, the O(1)—H hydroxyl group of the ethanol molecule participates in a hydrogen bond with the O(1*b*) carbonyl group at *x*, *y*, *z*. The *D*···*A* distances are 2·898 (6), 3·157 (6),

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² ×10³)

$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}.$$

	x	*y*	*z*	U_{eq}
Cl(1*a*)	5501 (1)	4150 (1)	1618 (1)	127 (2)
O(1*a*)	5934 (1)	521 (3)	1272 (1)	68 (2)
C(1*a*)	5529 (2)	−128 (4)	987 (2)	54 (2)
C(2*a*)	5536 (2)	−1366 (4)	791 (2)	60 (3)
C(3*a*)	5162 (1)	−2246 (4)	743 (2)	61 (2)
C(4*a*)	4622 (2)	−1636 (4)	357 (2)	63 (2)
N(5*a*)	4158 (1)	−81 (3)	411 (1)	57 (2)
C(6*a*)	3522 (2)	808 (4)	429 (2)	62 (3)
C(7*a*)	3277 (2)	1774 (4)	442 (2)	66 (3)
C(8*a*)	3471 (2)	2922 (4)	522 (2)	71 (3)
C(9*a*)	3921 (2)	3084 (4)	598 (2)	66 (3)
N(10*a*)	4584 (1)	2302 (3)	571 (2)	63 (2)
C(11*a*)	5084 (2)	1641 (4)	1021 (2)	58 (2)
C(12*a*)	5055 (1)	361 (3)	843 (2)	50 (2)
C(13*a*)	4627 (1)	−385 (4)	560 (2)	53 (2)
C(14*a*)	3962 (1)	962 (4)	480 (2)	54 (2)
C(15*a*)	4169 (2)	2111 (4)	564 (2)	57 (2)
C(16*a*)	5119 (2)	−3394 (4)	428 (2)	80 (3)
C(17*a*)	5363 (2)	−2549 (4)	1380 (2)	74 (3)
C(18*a*)	5302 (2)	1799 (4)	1676 (2)	65 (3)
C(19*a*)	5505 (2)	2890 (5)	1988 (3)	87 (4)
C(20*a*)	5709 (2)	3044 (6)	2572 (3)	119 (5)
C(21*a*)	5727 (3)	2071 (7)	2880 (3)	126 (5)
C(22*a*)	5532 (2)	982 (6)	2599 (2)	103 (4)
C(23*a*)	5321 (2)	853 (5)	2000 (2)	72 (3)
Cl(1*b*)	2608 (1)	9099 (1)	423 (1)	83 (1)
O(1*b*)	2966 (1)	4906 (3)	998 (2)	90 (3)
C(1*b*)	2656 (2)	4694 (4)	1087 (2)	68 (3)
C(2*b*)	2634 (2)	3447 (4)	1269 (2)	77 (4)
C(3*b*)	2458 (2)	3409 (4)	1641 (2)	73 (3)
C(4*b*)	1952 (2)	4142 (4)	1298 (2)	68 (3)
N(5*b*)	1666 (1)	6197 (3)	1101 (1)	54 (2)
C(6*b*)	1379 (2)	8101 (4)	1184 (2)	63 (3)
C(7*b*)	1232 (2)	9308 (4)	1020 (2)	74 (3)
C(8*b*)	1271 (2)	9835 (4)	627 (2)	75 (3)
C(9*b*)	1461 (2)	9191 (4)	397 (2)	63 (3)
N(10*b*)	1784 (1)	7298 (3)	306 (1)	54 (2)
C(11*b*)	2328 (1)	6836 (4)	775 (2)	57 (2)
C(12*b*)	2319 (1)	5628 (3)	1010 (2)	54 (2)
C(13*b*)	1990 (1)	5391 (3)	1129 (2)	52 (2)
C(14*b*)	1563 (1)	7439 (4)	951 (2)	50 (2)
C(15*b*)	1604 (1)	8000 (3)	550 (2)	50 (2)
C(16*b*)	2360 (3)	2118 (5)	1724 (4)	117 (6)
C(17*b*)	2886 (2)	3959 (5)	2269 (2)	101 (4)
C(18*b*)	2696 (1)	7780 (4)	1273 (2)	55 (2)
C(19*b*)	2842 (2)	8817 (4)	1161 (2)	61 (3)
C(20*b*)	3162 (2)	9673 (4)	1593 (2)	77 (3)
C(21*b*)	3343 (2)	9534 (5)	2178 (2)	84 (3)
C(22*b*)	3200 (2)	8515 (5)	2306 (2)	78 (3)
C(23*b*)	2886 (2)	7634 (4)	1871 (2)	67 (3)
O(1)	3592 (2)	6358 (5)	884 (2)	133 (3)
C(1)	4035 (5)	6666 (15)	1442 (5)	269 (12)
C(2′)	4141 (8)	6892 (17)	1919 (9)	192 (7)
C(2″)	4184 (10)	7739 (23)	1530 (13)	198 (9)

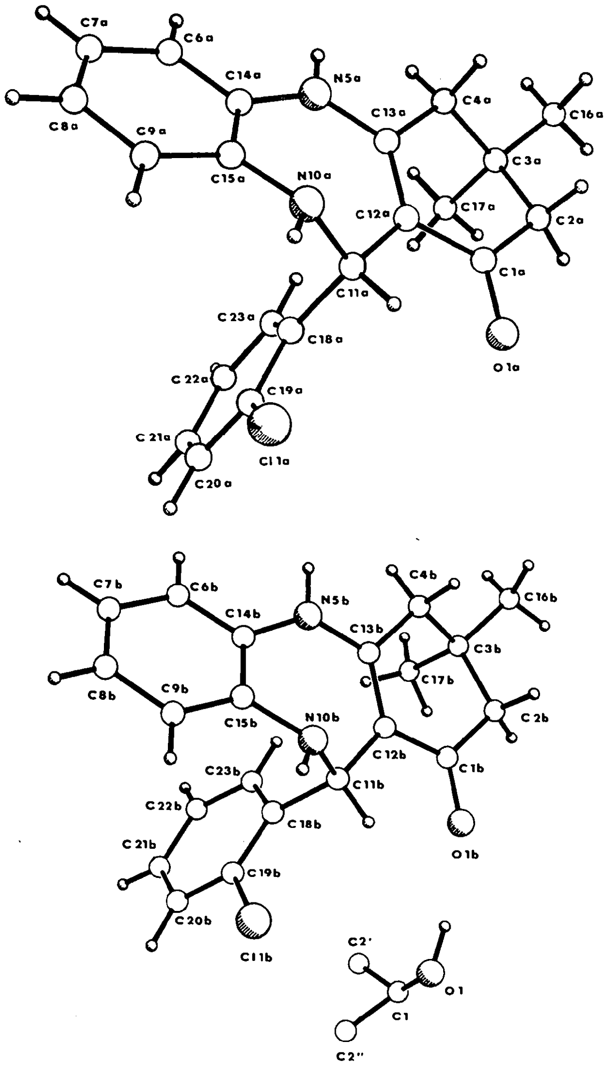

Fig. 1. Views of the two independent molecules showing the atom labelling. In the ethanol molecule, C(2′) and C(2″) depict partial occupancies of 0·55 (2) and 0·45 (2), respectively.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

Cl(1*a*)–C(19*a*)	1·748 (7)	Cl(1*b*)–C(19*b*)	1·756 (5)
O(1*a*)–C(1*a*)	1·254 (5)	O(1*b*)–C(1*b*)	1·242 (9)
C(1*a*)–C(2*a*)	1·486 (6)	C(1*b*)–C(2*b*)	1·494 (7)
C(1*a*)–C(12*a*)	1·458 (7)	C(1*b*)–C(12*b*)	1·435 (7)
C(2*a*)–C(3*a*)	1·517 (7)	C((2*b*)–C(3*b*)	1·528 (12)
C(3*a*)–C(4*a*)	1·529 (6)	C(3*b*)–C(4*b*)	1·522 (7)
C(3*a*)–C(16*a*)	1·513 (7)	C(3*b*)–C(16*b*)	1·517 (8)
C(3*a*)–C(17*a*)	1·529 (8)	C(3*b*)–C(17*b*)	1·526 (6)
C(4*a*)–C(13*a*)	1·497 (6)	C(4*b*)–C(13*b*)	1·497 (6)
N(5*a*)–C(13*a*)	1·374 (6)	N(5*b*)–C(13*b*)	1·367 (6)
N(5*a*)–C(14*a*)	1·403 (6)	N(5*b*)–C(14*b*)	1·411 (5)
C(6*a*)–C(7*a*)	1·361 (7)	C(6*b*)–C(7*b*)	1·392 (6)
C(6*a*)–C(14*a*)	1·392 (8)	C(6*b*)–C(14*b*)	1·382 (8)
C(7*a*)–C(8*a*)	1·373 (7)	C(7*b*)–C(8*b*)	1·358 (10)
C(8*a*)–C(9*a*)	1·388 (9)	C(8*b*)–C(9*b*)	1·380 (9)
C(9*a*)–C(15*a*)	1·399 (7)	C(9*b*)–C(15*b*)	1·370 (5)
N(10*a*)–C(11*a*)	1·478 (5)	N(10*b*)–C(11*b*)	1·484 (4)
N(10*a*)–C(15*a*)	1·395 (8)	N(10*b*)–C(15*b*)	1·420 (7)
C(11*a*)–C(12*a*)	1·486 (6)	C(11*b*)–C(12*b*)	1·506 (6)
C(11*a*)–C(18*a*)	1·531 (7)	C(11*b*)–C(18*b*)	1·538 (5)
C(12*a*)–C(13*a*)	1·369 (5)	C(12*b*)–C(13*b*)	1·376 (8)
C(14*a*)–C(15*a*)	1·390 (6)	C(14*b*)–C(15*b*)	1·398 (7)
C(18*a*)–C(19*a*)	1·389 (7)	C(18*b*)–C(19*b*)	1·366 (7)
C(18*a*)–C(23*a*)	1·376 (8)	C(18*b*)–C(23*b*)	1·406 (7)
C(19*a*)–C(20*a*)	1·357 (10)	C(19*b*)–C(20*b*)	1·361 (6)
C(20*a*)–C(21*a*)	1·372 (11)	C(20*b*)–C(21*b*)	1·383 (9)
C(21*a*)–C(22*a*)	1·357 (9)	C(21*b*)–C(22*b*)	1·365 (9)
C(22*a*)–C(23*a*)	1·386 (8)	C(22*b*)–C(23*b*)	1·383 (6)
O(1)–C(1)	1·340 (10)	C(1)–C(2′)	1·204 (33)
C(1)–C(2″)	1·246 (30)		

3·236 (4), 2·825 (8) Å and the H···*A* distances 2·03 (6), 2·39 (5), 2·79 (5), 1·95 (6) Å, respectively. The corresponding *D*—H···*A* angles are 161 (3), 161 (3), 145 (3), 149 (3)°.

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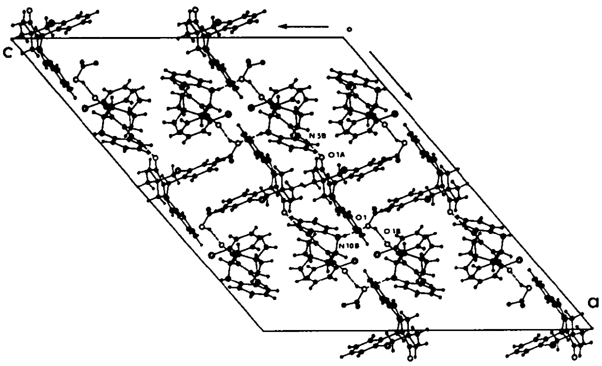

Fig. 2. The packing arrangement of the title compound as viewed along **b**. The dashed lines indicate hydrogen bonds.

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Structure of (3β,25*R*)-Spirost-5-ene-3,17-diol Hemihydrate (Pennogenin)*

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Abstract. $C_{27}H_{42}O_4.\frac{1}{2}H_2O$, $M_r = 439·6$, monoclinic, $P2_1$, $a = 18·880\ (8)$, $b = 7·446\ (2)$, $c = 19·911\ (7)$ Å, $\beta = 117·78\ (4)°$, $V = 2476\ (1)$ Å^3, $Z = 4$, $D_x = 1·18$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·073$ mm^{-1}, $F(000) = 964$, $T = 293$ K. Final $R = 0·047$ for 2575 observed reflections. The molecular structure is determined from the X-ray data and confirms the structure previously assigned on the basis of chemical and spectroscopic evidence. In the two independent molecules rings *A*, *C* and *F* have chair conformations and ring *B* adopts a half-chair conformation. The methyl substituents at the *A*/*B* and *C*/*D* ring junctions are *axial* and the ring *A* hydroxyl group and the ring *F*

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