

Comparison with other derivatives of lupinine (Table 3) shows that (i) neither N protonation nor any substituent on the C(11) atom causes inversion of the *trans*-quinolizidine, (ii) N alkylation leads to conformational and configurational changes in the lupinine molecule, (iii) the substituent at the C(1) atom in the equatorial orientation is chemically more stable than the axial one [R. K. Hill in Pelletier (1970)] and more susceptible to intermolecular interactions in the solid state.

Bond lengths and angles (Table 2) are as expected. The mean N^+-C bond distance of 1.517 (7) Å is in good agreement with values found for quaternary amino salts.

In the crystal structure (Fig. 2) cations and anions are linked together by the interionic $O-H\cdots I^-$ hydrogen bonds and by electrostatic $N^+-CH_3\cdots I^-$ attractions.

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Antischistosomal Analogs of Hycanthone. III.* Structure of the 1:1 Chloroform Solvate of 8-Chloro-2-[2-(diethylamino)ethyl]-2H-[1]benzothiopyrano[4,3,2-*cd*]indazole-5-methanol, $C_{20}H_{22}ClN_3OS \cdot CHCl_3$ †

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Abstract. $M_r = 507.312$, monoclinic, $P2_1/n$, $a = 10.312$ (1), $b = 30.502$ (2), $c = 8.683$ (1) Å, $\beta = 120.046$ (6)°, $V = 2364.1$ Å³, $Z = 4$, $D_x = 1.425$ g cm⁻³, $\lambda(Cu K\alpha_1) = 1.54056$ Å, $\mu = 54.93$ cm⁻¹, $F(000) = 1046$, $T = 296$ (1) K. Final $R(F) = 0.056$ for 2865 counter reflections. All H atoms were located and their parameters refined. Bond lengths and angles are all within the ranges of expected values, and the fused four-ring system is nearly planar. The terminal N atom is not protonated and is hydrogen bonded to the H atom of the chloroform molecule *via*

$N\cdots H-C$, with $N\cdots H$ distance 2.31 (4) Å and $N\cdots H-C$ angle 160 (3)°. The ring nitrogen, not connected to the side chain, acts as an acceptor in a $N\cdots H-O$ hydrogen bond with a neighboring translation-related molecule, while the hydroxyl O atom in turn donates its H atom to the same N atom of another translation-related molecule, thus forming an infinite hydrogen-bonded chain in the [101] direction, the $N\cdots H$ length and $N\cdots H-O$ angle being 2.03 (6) Å and 163 (5)°, respectively. In the chloroform molecule, the average C-Cl and Cl \cdots Cl distances are 1.753 (3) and 2.881 (1) Å; the average Cl-C-Cl angle is 110.6 (2)°. Stereochemical evidence suggests two alternative configurations for the $-CH_2OH$ group having different occupancies (ratio roughly 9:1).

* Part II: Wei (1982).

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References

- CROW, W. (1958). *Aust. J. Chem.* **11**, 366–371.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JASKÓLSKI, M. (1979). PhD Dissertation, A. Mickiewicz Univ., Poznań.
 KOZIOŁ, A. E., GDANIEC, M. & KOSTURKIEWICZ, Z. (1980a). *Acta Cryst.* **B36**, 980–981.
 KOZIOŁ, A. E., GDANIEC, M. & KOSTURKIEWICZ, Z. (1980b). *Acta Cryst.* **B36**, 982–983.
 KOZIOŁ, A. E. & KOSTURKIEWICZ, Z. (1980). *Acta Cryst.* **B36**, 2483–2485.
 KOZIOŁ, A. E., KOSTURKIEWICZ, Z. & PODKOWIŃSKA, H. (1978). *Acta Cryst.* **B34**, 3491–3494.
 KOZIOŁ, A. E. & PODKOWIŃSKA, H. (1983). *Acta Cryst.* **C39**, 1373–1374.
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
 OHRT, J., PARTHASARATHY, R., LA LONDE, R. T. & WONG, C. F. (1973). *J. Cryst. Mol. Struct.* **3**, 3–13.
 PELLETIER, S. W. (1970). *Chemistry of Alkaloids*, pp. 414–417. New York: Van Nostrand-Reinhold.
 SADYKOV, A. S., ASLANOV, KH. A. & KUSHMURADOV, YU. K. (1975). *Alkaloidy Khinolizidinovogo Ryada: Khimya Stereokhimya Biogenez*, p. 201. Moscow: Nauka.
 SKOLIK, J., KRUEGER, P. J. & WIEWIÓROWSKI, M. (1968). *Tetrahedron*, **24**, 5439–5456.
 Syntex XTL (1973). *Operation Manual*. Cupertino: Syntex Analytical Instruments.

Introduction. Hycanthonone is a drug still widely used for the treatment of schistosomiasis despite its potential risks to human health suggested by the carcinogenic, mutagenic and teratogenic activities observed in experimental animals and bacteria (Bueding & Batzinger, 1977). Chemical alterations of the thioxanthenone framework of hycanthonone to benzothioapyrano-indazole-type derivatives, however, was reported by Bueding (1975) to yield marked reduction in mutagenic activity without decreasing antischistosomal potency. Among these derivatives, the chloroindazole analog of hycanthonone, designated IA-4 (Bueding, Fisher & Bruce, 1973), has also been shown to be much less toxic than hycanthonone (Bueding, Fisher & Bruce, 1973; Bueding, 1975).

In the preceding papers X-ray structural studies of hycanthonone methanesulfonate (Wei & Einstein, 1978), IA-4 methanesulfonate (Wei, 1981), and dechloro IA-4 monohydrate (Wei, 1982) have been reported from this laboratory. The results showed that the thioxanthenone ring system of hycanthonone and the benzothioapyrano-indazole ring system of the two hycanthonone derivatives are nearly planar and that the terminal N of the side chain forms either a N—H···O or a N···H—O H-bond with a neighboring anion or hydroxyl group. The terminal N and the —CH₂OH group of each of these drugs allow the molecule to act as a 'double-headed' link in the formation of infinite intermolecular H-bond networks. Facile formation of a H-bond for the terminal N is a basis of the hypothesis in which the interaction of the drug with a phosphate group at the periphery of the DNA helix is thought to account for the stability of the drug-DNA complex (for review, see Weinstein & Hirschberg, 1971; Hirschberg, 1975).

Although two chemically different types of new antischistosomal drugs, *p*-(*p*-nitroanilino)phenyl isothiocyanate (amoscanate) and 4-methyl-5-(2-pyrazinyl)-3*H*-1,2-dithiole-3-thione (oltipraz), have recently been developed for eventual clinical use and their X-ray structures reported (Hardgrove Jr, Einstein & Wei, 1983; Wei, 1983), the therapeutic value of hycanthonone analogs cannot be totally ruled out.

Our continued efforts to elucidate structure-function relationships of hycanthonone analogs have now resulted in additional stereochemical information for one of the least toxic members in the form of its 1:1 chloroform adduct.

Experimental. A white powder sample of IA-4 base was kindly furnished by Professor Ernest Bueding; attempts to crystallize the compound from 95% ethanol solution only produced thin coiled strips from which a piece was cut and used to determine crystal data: monoclinic, $P2_1/c$, $a = 23.64$ (2), $b = 9.72$ (1), $c = 8.58$ (2) Å, $\beta = 95.1$ (1)°. Because diffraction only extended to 2θ value of roughly 60° and mosaic spread was as much as 4°, data collection from this crystal was abandoned.

Useful chunky crystals in the form of hexagonal rods were grown at 277 K from chloroform solution; crystals kept at room temperature gradually became opaque and amorphous. A crystal with approximate dimensions 0.58 × 0.25 × 0.18 mm was first soaked in chloroform-soluble, transparent epoxy resin (E.Pox.E 5 glue, product of Loctite Corp.) and sealed at 277 K in a thin glass capillary; this treatment fixed the crystal inside the capillary without decay and enabled data collection at room temperature.

Crystal mounted on a Picker four-circle diffractometer with c approximately parallel to ϕ axis of diffractometer; angle measurements of 12 strong reflections in 2θ range 92–107° used in least-squares refinement of lattice parameters (Busing, Ellison, Levy, King & Roseberry, 1968) which yielded the parameters given in the *Abstract*; systematic absences $h0l$ $h + l = 2n + 1$, $0k0$ $k = 2n + 1$ consistent with $P2_1/n$. Because of slight movement of crystal its orientation angles were redetermined several times during data collection in a manner similar to data collection for protein crystals. θ - 2θ step scans, 2θ range 1–120° ($-11 \leq h \leq 10$, $0 \leq k \leq 34$, $0 \leq l \leq 9$). 3068 unique nonzero reflections, of which 203 with $F_o^2 < \sigma(F_o^2)$ excluded from final least-squares refinement; absorption corrections (0.885 to 1.000) applied empirically from a transmission curve obtained by measuring intensities of 004 reflection for rotation angles at 10° intervals about its reciprocal-lattice vector; maximum mosaic spread of crystal estimated to be 0.5°.

Structure solved with *MULTAN* (Germain, Main & Woolfson, 1971) using four reflections in starting set of 300 reflections with largest E values; preliminary refinement for 30 non-H atoms carried out using block-diagonal least-squares program of Shiono (1971), giving $R(F)$ value 0.086 (all atoms anisotropic). By iterative least-squares refinements and difference-Fourier syntheses all 23 H atoms finally located and included in refinement with isotropic B values [$R(F) = 0.061$]; four cycles of least-squares refinement on F^2 [full-matrix program *ORXFLS4* (Busing, Martin & Levy, 1962)] yielded $R(F) = 0.057$. Highest residual peak (0.44 e Å⁻³) persistently appeared in difference-Fourier syntheses, roughly 1 Å away from the hydroxyl O atom, suggesting either coexistence of —CH₂OH and —CHO moieties, as found for structure of hycanthonone methanesulfonate (Wei & Einstein, 1978), or two alternative orientations for the —CH₂OH moiety; the former possibility rejected on the basis of stereochemical consideration. In final four cycles of refinement —CH₂OH group treated as partially disordered (major sites with occupancy factor m ; minor hydroxyl O atom site with occupancy factor $1 - m$); scattering factors from Cromer & Waber (1974); anomalous-scattering corrections for S and Cl from Cromer (1974); $w^{-1} = \sigma^2(F_o^2)$, $\sigma^2(F_o^2)$ estimated according to empirical expression given elsewhere (Wei & Einstein,

1978); H atoms and minor O sites treated isotropically and non-H atoms anisotropically. On final cycle Δ/σ for non-H atoms <0.02 ; maximum Δ in H parameters 0.05σ . For 2865 reflections used in refinement, $R(F) = 0.056$, $R(F^2) = 0.071$, $wR(F^2) = [\sum w|\Delta F^2|^2 / \sum wF_o^4]^{1/2} = 0.128$, $m = 0.91$ (1), and $S = 1.80$ {defined as $[\sum w|\Delta F^2|^2 / (n-p)]^{1/2}$ where n is the number of observations and p is the number of

variables; data-to-variable ratio 7.79}. With all 3068 unique nonzero reflections included, $R(F) = 0.060$; final difference Fourier showed maximum $\Delta\rho = 0.42 \text{ e } \text{Å}^{-3}$.

Discussion. Positional parameters and isotropic temperature factors (or their equivalents) are listed in Table 1.*

The crystal structure is composed of neutral chloroform-solvated molecules linked together by H-bonds (see below). To each IA-4 base, a chloroform molecule is attached through the formation of a C—H...N bond. Fig. 1 gives bond lengths and bond angles for the solvated molecule together with their corresponding e.s.d.'s. This and the following figure were prepared with the program ORTEP II (Johnson, 1976); molecular parameters were calculated by the program ORFFE4 (Busing, Martin & Levy, 1964).

All bond lengths and angles for non-H atoms of the fused-ring system appear normal and are close to those found for the analogous molecules of IA-4 cation (Wei, 1981) and dechloro IA-4 base (Wei, 1982). All 22 C—H distances and one O—H distance range from 0.86 (4) Å [for C(2)—H(2)] to 1.11 (5) Å [for C(17)—H(17b)], with an average value of 0.96 Å. The

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, and two figures illustrating (a) two alternative configurations for the hydroxyl group and (b) a stereoscopic view of the solvated molecule, showing the numbering scheme for H atoms and thermal ellipsoids for non-H atoms, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38595 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and isotropic thermal parameters

The e.s.d.'s are given in parentheses in all tables and in the text. The digits in parentheses correspond to the least significant digits of the parameters. The equivalent isotropic temperature factors for C, N, O, Cl and S atoms were calculated from the corresponding anisotropic thermal parameters and unit-cell parameters by the relation $B_{\text{eq}} = \frac{1}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$ (Hamilton, 1959).

	x	y	z	B_{eq} Or $B(\text{Å}^2)$
S	0.6946 (1)	0.53670 (3)	0.8306 (1)	4.07 (3)
Cl(1)	0.4359 (1)	0.65955 (4)	0.3287 (2)	5.99 (5)
Cl(2)	0.0534 (1)	0.36212 (4)	1.0792 (2)	6.79 (5)
Cl(3)	0.3056 (2)	0.31259 (5)	1.1199 (2)	9.08 (7)
Cl(4)	0.0186 (3)	0.27049 (6)	0.9804 (2)	10.84 (10)
C(1)	0.4392 (4)	0.4387 (1)	0.8451 (5)	3.6 (1)
C(2)	0.5337 (4)	0.4137 (1)	0.9943 (5)	4.4 (1)
C(3)	0.6802 (4)	0.4278 (1)	1.0899 (5)	4.3 (1)
C(4)	0.7383 (4)	0.4648 (1)	1.0479 (5)	3.9 (1)
C(5)	0.5409 (5)	0.5929 (1)	0.5649 (5)	4.1 (2)
C(6)	0.4183 (4)	0.6102 (1)	0.4172 (5)	4.3 (2)
C(7)	0.2799 (5)	0.5896 (1)	0.3397 (6)	4.7 (2)
C(8)	0.2656 (4)	0.5517 (1)	0.4131 (5)	4.4 (2)
C(9)	0.3716 (4)	0.4932 (1)	0.6464 (4)	3.4 (1)
C(10)	0.4931 (4)	0.4755 (1)	0.8014 (5)	3.4 (1)
C(11)	0.6412 (4)	0.4894 (1)	0.9016 (5)	3.6 (1)
C(12)	0.5265 (4)	0.5542 (1)	0.6403 (5)	3.4 (1)
C(13)	0.3854 (4)	0.5330 (1)	0.5641 (5)	3.6 (1)
C(14)	0.8997 (4)	0.4777 (2)	1.1609 (7)	4.8 (2)
C(15)	0.1810 (5)	0.4036 (1)	0.7038 (6)	4.3 (2)
C(16)	0.1851 (5)	0.3625 (2)	0.6134 (8)	4.9 (2)
C(17)	0.1241 (8)	0.2847 (2)	0.6164 (9)	7.3 (3)
C(18)	0.1396 (16)	0.2684 (3)	0.4641 (17)	10.9 (6)
C(19)	−0.0737 (5)	0.3403 (2)	0.4525 (8)	6.1 (2)
C(20)	−0.1989 (8)	0.3156 (3)	0.4535 (14)	7.7 (3)
C(21)	0.1098 (6)	0.3192 (2)	0.9906 (7)	6.0 (2)
N(1)	0.2903 (3)	0.4358 (1)	0.7182 (4)	4.0 (1)
N(2)	0.0743 (4)	0.3305 (1)	0.6020 (4)	4.5 (1)
N(3)	0.2491 (3)	0.4691 (1)	0.5944 (4)	3.9 (1)
O*	0.9851 (4)	0.4436 (1)	1.2707 (8)	6.6 (2)
H(2)	0.504 (4)	0.391 (1)	1.029 (5)	3.8 (8)
H(3)	0.744 (4)	0.411 (1)	1.191 (5)	3.7 (8)
H(5)	0.628 (4)	0.606 (1)	0.614 (5)	3.9 (8)
H(7)	0.197 (4)	0.601 (1)	0.226 (5)	4.2 (8)
H(8)	0.167 (5)	0.535 (1)	0.360 (5)	5.8 (10)
H(14a)*	0.941 (5)	0.481 (2)	1.088 (6)	4.9 (11)
H(14b)*	0.916 (6)	0.503 (2)	1.221 (7)	6.3 (14)
H(15a)	0.204 (4)	0.398 (1)	0.820 (5)	3.8 (9)
H(15b)	0.086 (5)	0.418 (1)	0.638 (5)	5.0 (9)
H(16a)	0.274 (6)	0.350 (2)	0.683 (6)	6.0 (12)
H(16b)	0.175 (5)	0.369 (1)	0.499 (6)	5.2 (10)
H(17a)	0.047 (7)	0.265 (2)	0.615 (7)	8.8 (16)
H(17b)	0.242 (6)	0.274 (2)	0.699 (7)	7.7 (13)
H(18a)	0.207 (10)	0.286 (3)	0.451 (12)	13.5 (31)
H(18b)	0.184 (10)	0.238 (3)	0.522 (11)	14.2 (28)
H(18c)	0.052 (12)	0.272 (4)	0.332 (16)	18.3 (43)
H(19a)	−0.090 (5)	0.371 (2)	0.465 (6)	6.3 (12)
H(19b)	−0.076 (6)	0.333 (2)	0.339 (7)	7.7 (14)
H(20a)	−0.189 (7)	0.285 (2)	0.443 (8)	10.0 (19)
H(20b)	−0.180 (9)	0.315 (2)	0.569 (11)	12.3 (28)
H(20c)	−0.295 (8)	0.324 (2)	0.356 (9)	9.8 (18)
H(21)	0.092 (4)	0.330 (1)	0.877 (5)	4.3 (9)
H(O)*	1.067 (7)	0.455 (2)	1.354 (8)	7.3 (15)
O†	0.950 (3)	0.460 (1)	1.338 (3)	2.6 (9)

* Atoms of major configuration each with an occupancy factor of 0.91 (1) (see text).

† Hydroxyl O atom of minor configuration with an occupancy factor of 0.09 (1) (see text).

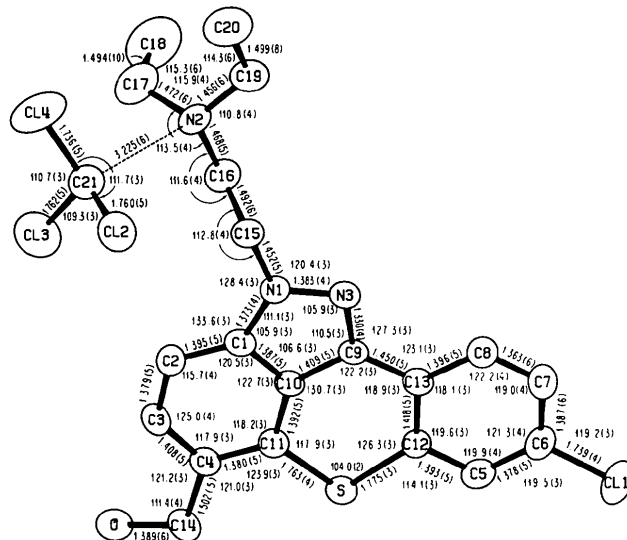


Fig. 1. Bond lengths (Å) and bond angles (°) with their e.s.d.'s for non-H atoms of the 1:1 chloroform adduct of IA-4.

H—C—C angles for the five ring H atoms are within two e.s.d.'s of 120° (e.s.d.'s are all 2°). The H(O)—O—C(14) angle is 107 (4)°, and the remaining 37 H—C—C, H—C—N and H—C—H angles are in the range of 85 (3)° [for H(17*b*)—C(17)—C(18)] to 124 (3)° [for H(17*b*)—C(17)—N(2)], the average value being 109°.

The long side chain has a conformation similar to that observed for dechloro IA-4 base (Wei, 1982), as can be visualized by comparison of various torsion angles shown in Table 2(a). As expected, atoms of the terminal methyl groups exhibit large thermal motions. This agrees with previous observations made for the structures of this family of drugs (Wei & Einstein, 1978; Wei, 1981, 1982).

Calculations of various least-squares planes for the fused four-ring heterocyclic framework show that all C atoms of each of the two outer six-membered rings are coplanar to within 0.010 (3) Å, whereas C(9) and S are much further from these planes [e.g. C(9) is 0.034 (5) Å out of the plane formed by C(5), C(6), C(7), C(8), C(13) and C(12)]. The five-membered ring is essentially planar, the maximum deviation from this plane being that of N(3), -0.006 (2) Å. The angles between the planes of the two outer six-membered rings, and between the plane of the five-membered ring and the planes of the two outer six-membered rings and the plane of the fused three six-membered ring system range from 177.2 (1) to 179.5 (2)°, indicating that the whole fused four-ring system is approximately planar.

Table 2. *Molecular parameters*

(a) Comparison of torsion angles (°) involving side-chain atoms. The torsion angle of a chain of atoms *A*, *B*, *C* and *D* is defined as the angle that the projection of bond *A—B* makes relative to the bond *C—D* when viewed along the direction *B—C*. The sign is positive if a clockwise motion of atom *A* would move it toward atom *D* (Klyne & Prelog, 1960).

<i>A—B—C—D</i>	IA-4 cation*	Dechloro IA-4 base†	This work
C(15)—N(1)—C(1)—C(2)	-4.0 (7)	-1.4 (3)	0.8 (7)
C(16)—C(15)—N(1)—C(1)	175.1 (3)	-90.1 (3)	-83.7 (6)
N(2)—C(16)—C(15)—N(1)	77.3 (5)	175.6 (2)	179.5 (4)
C(17)—N(2)—C(16)—C(15)	77.8 (4)	-154.5 (2)	-146.1 (5)
C(19)—N(2)—C(16)—C(15)	-157.6 (4)	76.1 (3)	81.5 (5)
C(18)—C(17)—N(2)—C(16)	58.6 (5)	-61.7 (3)	-67.7 (8)
C(20)—C(19)—N(2)—C(16)	83.3 (6)	-164.4 (3)	-167.5 (5)

(b) H-bonds and chloroform molecule.

(i) H-bonds (*A—H...B*)

<i>A</i>	<i>H</i>	<i>B</i>	<i>A...B</i>	<i>A—H</i>	<i>H...B</i>	∠ <i>A—H...B</i>
C(21)	H(21)	N(2)	3.225 (6) Å	0.96 (4) Å	2.31 (4) Å	160 (3)°
O	H(O)	N(3)‡	2.874 (5)	0.87 (6)	2.03 (6)	163 (5)

(ii) Intramolecular distances and angles of chloroform (not shown in Fig. 1)

C(2)···C(3)	2.873 (2) Å	H(21)—C(21)—C(2)	105 (2)°
C(3)···C(4)	2.878 (3)	—C(3)	105 (2)
C(4)···C(2)	2.893 (2)	—C(4)	115 (2)
	av. 2.881 (1)		av. 108 (1)

* Wei (1981).

† Wei (1982).

‡ Symmetry code: 1 + *x*, *y*, 1 + *z*.

Unlike methanesulfonate salts of hycanthone and IA-4, the terminal N(2) atom in this structure is not protonated. However, the H atom of the chloroform molecule points toward this 'H-hungry' tetrahedral atom so that a C(21)—H(21)···N(2) bond is formed. The distance between H(21) and N(2) is 2.31 (4) Å, considerably shorter than the 2.7 Å sum of the van der Waals radii for H and N (Pauling, 1960). The C(21)···N(2) contact of 3.225 (6) Å can be compared with 3.287 (16) Å found for triphenyltelluronium cyanate—chloroform(1/2) (Titus, Lee & Ziolo, 1976). This H-bond is rather a weak one, accounting for the easy loss of chloroform when the solvated compound was kept at room temperature, thus resulting in an amorphous mass. Further, N(2) is displaced from the plane formed by C(16), C(17) and C(19) by 0.384 (5) Å, much less than the 0.422 (2) Å found in the hycanthone cation, 0.432 (4) Å in the IA-4 cation, and 0.413 (2) Å in the dechloro IA-4 monohydrate. It seems reasonable that when N(2) with a lone pair of electrons is protonated, the anion with high electron density interacts strongly with the H atom so as to cause a greater deviation of N(2) from the basal three-atom plane than in nonprotonated cases.

A close stereochemical examination of the geometry surrounding the perplexing highest residual peak, O', found in the neighborhood of the hydroxyl O atom, led to the deduction that the -CH₂OH group is partially disordered. Results of the refinement yielded the following parameters: C(14)—O' 1.46 (2) Å; O···O' 0.96 (3) Å; C(4)—C(14)—O' 106 (1)°; O—C(14)—O' 39 (1)°. Although 1.46 (2) Å for C(14)—O' is longer than the expected value of 1.426 (5) Å in a -CH₂OH group (Sutton, 1965), 106 (1)° for C(4)—C(14)—O' is much closer to the tetrahedral angle than the trigonal one. The final *R*(*F*²) values for ordered and partially disordered models were not significantly different, being 0.073 and 0.071, respectively. Still, the unbiased disordered model was chosen in this paper. Since the occupancy factor of 0.09 (1) was obtained for O', attempts were not made to incorporate in the refinement the minor sites for the three H atoms. Their contributions to structure factors were considered to be negligible.

Because of the inability of N(2) to form infinite intermolecular H-bonds, as in the three above-mentioned hycanthone analogs, the present structure finds as its secondary choice the formation of a one-dimensional H-bond chain, using N(3). Atom N(3) acts as an acceptor of H(O) attached to the translation-related (*x* - 1, *y*, *z* - 1) O atom of a neighboring IA-4 base, and the O atom of the same molecule is further H-bonded to another N(3) of the IA-4 base related to the reference one by translations *x* + 1, *y*, *z* + 1. Thus, each IA-4 base is connected to two neighboring IA-4 bases, forming an infinite chain *via* N(3)···H(O)—O H-bonds in the [101] direction. This type of H-bond

network differs from those for the other three analogous drugs in which both N(2) and hydroxyl O are engaged in 'double-headed' fashion in the formation of infinite intermolecular H-bonding [N(2)—H...O and O—H...O for the hycanthonc cation and the IA-4 cation; N(2)...H—O and O—H...N(2) for the dechloro IA-4 monohydrate]. It is noteworthy that each of the four structures investigated so far invariably forms infinite intermolecular H-bonding but in different ways. The parameters of the two H-bonds involved in this structure are shown in Table 2(b).

Many organometallic and organic structures containing chloroform molecules have been reported to date. The structural role of this solvent is merely to occupy space in crystal lattices or to stabilize the compounds by forming weak H-bonds (van Soest & Peerdeman, 1970). In these structures, chloroform molecules were observed to have large thermal motion (Wilford, Smith & Powell, 1968; Preston & Kennard, 1969; Schaefer & Marsh, 1969; Park, Collins & Hoard, 1970; Lauher & Ibers, 1974; Wang, Huie & Schaefer, 1979), partially disordered configurations (Summerville, Cohen, Hatano & Scheidt, 1978; Johnson & Scheidt, 1978; Davis & Einstein, 1978), or both (Hall, Rae & Waters, 1967). In some cases, even the stoichiometric ratios of chloroform to compound were not precisely defined (Pettersen, Birnbaum, Ferguson, Islam & Sime, 1968; Mason & Towl, 1970; Wang, Huie & Schaefer, 1979).

In the present structure, the Cl atoms of the chloroform molecule do exhibit large thermal motion but are not disordered, conceivably because of the weak H-bond between the chloroform H atom and N(2). Atom C(21) lies 0.552 (5) Å out of the plane formed by the three Cl atoms. The observed average C(21)—Cl distance of 1.753 (3) Å and average Cl—C(21)—Cl angle of 110.6 (2)° can be compared with 1.762 Å and 110.9° obtained from a microwave investigation of chloroform (Wolfe, 1956). A survey of these parameters in chloroform-solvated complexes reveals that they range widely from 1.64 (3) Å (Lauher & Ibers, 1974) to 1.83 (6) Å (Watenpaugh & Caughlan, 1967) for C—Cl; from 100 (6)° (Wilford, Smith & Powell, 1968) to 116 (2)° (Lauher & Ibers, 1974) for Cl—C—Cl. Other pertinent parameters involving those for the chloroform molecule in the present structure are given in Table 2(b).

Fig. 2 shows the [001] projection of the unit cell. There are stacking interactions at a distance of 3.480 (2) Å between the nearly planar, fused four-ring systems of pairs of molecules related by centers of symmetry. The closest intermolecular contact between non-H atoms is 3.256 (7) Å for Cl(2)...O, and that between non-H and H atoms is 2.85 (4) Å for Cl(2)...H(7).

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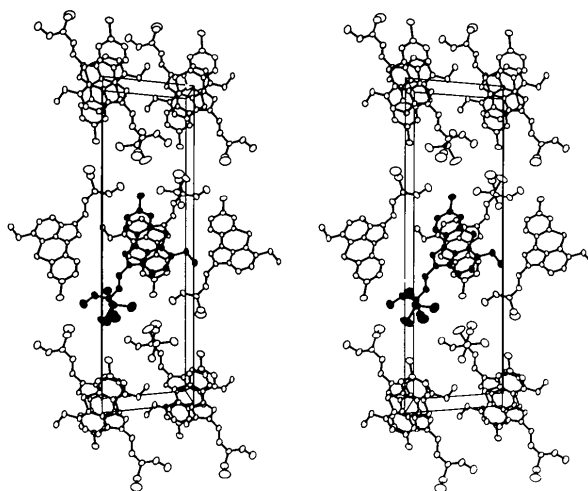


Fig. 2. Stereoscopic pair showing the [001] projection of the unit cell. The axial system is right handed. For the sake of clarity, H atoms are not included, and six IA-4 and two chloroform molecules partly contained inside the unit cell are eliminated. Darkened atoms are those for the reference solvated molecule. The origin of the unit cell is in the lower left rear corner.

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References

- BUEDING, E. (1975). *J. Toxicol. Environ. Health*, **1**, 329–334.
 BUEDING, E. & BATZINGER, R. P. (1977). *Origins of Human Cancer*, edited by H. H. HIATT, S. D. WATSON & A. WINSTEN, pp. 445–463. New York: Cold Spring Harbor Laboratory.
 BUEDING, E., FISHER, J. & BRUCE, J. (1973). *J. Pharmacol. Exp. Ther.* **186**, 403–407.
 BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). *The Oak Ridge Computer-Controlled X-ray Diffractometer*. Report ORNL-4143. Oak Ridge National Laboratory, Tennessee.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
 CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, p. 149, Table 2.3.1. Birmingham: Kynoch Press.
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 72–75, Table 2.2A. Birmingham: Kynoch Press.
 DAVIS, A. R. & EINSTEIN, F. W. B. (1978). *Acta Cryst.* **B34**, 2110–2115.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

- HALL, D., RAE, A. D. & WATERS, T. N. (1967). *Acta Cryst.* **22**, 258–268.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HARDGROVE, G. L. JR, EINSTEIN, J. R. & WEI, C. H. (1983). *Acta Cryst.* **C39**, 616–620.
- HIRSCHBERG, E. (1975). *Antibiotics*. Vol. 3. *Mechanism of Action of Antimicrobial and Antitumor Agents*, edited by J. W. CORCORAN & F. E. HAHN, pp. 274–303. Berlin: Springer.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- JOHNSON, J. F. & SCHEIDT, W. R. (1978). *Inorg. Chem.* **17**, 1280–1287.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- LAUHER, J. W. & IBERS, J. A. (1974). *J. Am. Chem. Soc.* **96**, 4447–4452.
- MASON, R. & TOWL, A. D. C. (1970). *J. Chem. Soc. (A)*, pp. 1601–1613.
- PARK, J. J., COLLINS, D. M. & HOARD, J. L. (1970). *J. Am. Chem. Soc.* **92**, 3636–3644.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
- PETTERSON, R. C., BIRNBAUM, G. I., FERGUSON, G., ISLAM, K. M. S. & SIME, J. G. (1968). *J. Chem. Soc. (B)*, pp. 980–984.
- PRESTON, H. S. & KENNARD, C. H. L. (1969). *J. Chem. Soc. (A)*, pp. 2682–2685.
- SCHAEFER, W. P. & MARSH, R. E. (1969). *Acta Cryst.* **B35**, 1675–1682.
- SHIONO, R. (1971). *Crystallographic Computing Program for IBM 1130*. Tech. Rep. No. 49. Department of Crystallography, Univ. of Pittsburgh, Pennsylvania.
- SOEST, T. C. VAN & PEERDEMAN, A. F. (1970). *Acta Cryst.* **B26**, 1940–1947.
- SUMMERVILLE, D. A., COHEN, I. A., HATANO, K. & SCHEIDT, W. P. (1978). *Inorg. Chem.* **17**, 2906–2910.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Spec. Publ. No. 18, edited by L. E. SUTTON, p. S 20s. London: The Chemical Society.
- TITUS, D. D., LEE, J.-S. & ZIOLO, R. F. (1976). *J. Organomet. Chem.* **120**, 381–388.
- WANG, B.-C., HUIE, B. T. & SCHAEFER, W. P. (1979). *Acta Cryst.* **B35**, 1232–1234.
- WATENPAUGH, K. & CAUGHLAN, C. N. (1967). *Inorg. Chem.* **6**, 963–967.
- WEI, C. H. (1981). *Acta Cryst.* **B37**, 844–849.
- WEI, C. H. (1982). *Acta Cryst.* **B38**, 548–553.
- WEI, C. H. (1983). *Acta Cryst.* **C39**, 1079–1082.
- WEI, C. H. & EINSTEIN, J. R. (1978). *Acta Cryst.* **B34**, 205–212.
- WEINSTEIN, I. B. & HIRSCHBERG, E. (1971). *Progress in Molecular and Subcellular Biology*, Vol. 2, edited by F. E. HAHN, pp. 232–246. Berlin: Springer.
- WILFORD, J. B., SMITH, N. O. & POWELL, H. M. (1968). *J. Chem. Soc. (A)*, pp. 1544–1549.
- WOLFE, P. N. (1956). *J. Chem. Phys.* **25**, 976–981.

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Désoxy-1 Méthyl-1 α -D-Glucopyranose, C₇H₁₄O₅

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Abstract. $M_r = 178.2$, orthorhombic, $P2_12_12_1$, $a = 15.053$ (8), $b = 10.758$ (5), $c = 5.102$ (2) Å, $V = 827.63$ Å³, $Z = 4$, $D_x = 1.43$ Mg m⁻³, Mo K α , $\lambda = 0.71069$ Å, $T = 298$ K, $F(000) = 384$, $R = 3\%$ for 1421 reflexions. The pyranose ring has the ⁴C₁ conformation. The effect of the 1-methyl group on the intermolecular interactions is discussed.

Introduction. La molécule de C₇H₁₄O₅ (Fig. 1) a été synthétisée au Laboratoire du Professeur Sinay à Orléans (Poungny, Mahmoud Nassr & Sinay, 1981). Il s'agissait pour ces auteurs de déterminer sans ambiguïté si le méthyle substitué directement sur le carbone anomérique C(1) du cycle était en position axiale ou équatoriale, ce que les études par RMN n'avaient pu déterminer. Il était d'autre part intéressant d'étudier les modifications éventuelles d'un cycle pyranique quand l'oxygène est remplacé par un carbone.

Partie expérimentale. Cristal 1,50 × 0,50 × 0,1 mm, 25 réflexions trouvées pour la recherche automatique de la maille; 1421 réflexions indépendantes mesurées sur diffractomètre Philips PW1100 {75 considérées comme

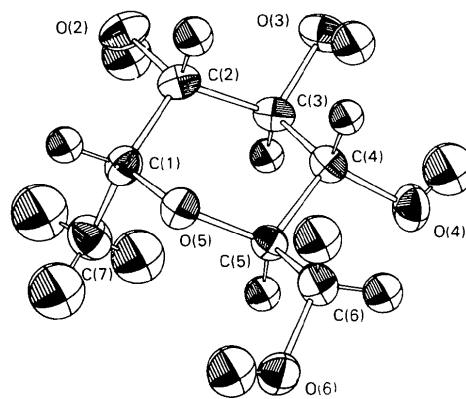


Fig. 1. Vue en perspective de la molécule.

inobservées [$3\sigma(I) \geq I$], avec $2\theta_{\max} = 60^\circ$, $h_{\max} = 22$, $k_{\max} = 16$, $l_{\max} = 8$; trois réflexions standards mesurées toutes les deux heures (variation négligeable). L'instabilité: 0,004. 1226 réflexions mesurées deux fois avec $R_{\text{int}} = 0,021$; pas de correction pour extinction secondaire. L'absorption ayant été négligée, les phases de 106 facteurs normalisés E , tels que $|E| \geq 1,72$, ont