atom has a significant deviation from a sp^2 planar hybridization. In the β form, however, the C(5) atom deviates in the opposite direction. The deviation of the N(1) atom from the plane defined by the C(11), N(2) and C(5) atoms is 0·214 (0·023) Å. Therefore, the nonplanarity of the diphenylpyrazoline moiety is more manifest in the α form. The reason is not obvious at present, but the intra- and intermolecular interactions which cause the different conformations of the three phenyl groups in the two forms must be related to this observation.

The molecular packing in the unit cell viewed along the normal to the PYR plane is shown in Fig. 3. The intermolecular distances, which are close to the sum of van der Waals radii in the α form, are as follows: Cl···H(36) at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ 2·88 (3) Å, H(55)···C(36) at $(2-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ 2·89 (3) Å, C(15)···H(4*B*) at $(1-x, 1-y, -z)$ 2·96 (3) Å. These contacts may account for the rotation of each phenyl group. Similarly, the short contacts found in the β form are: Cl···H(12) at $(1-x, 1-y, 1-z)$ 2·95 (6) Å, C(16)···H(4*B*) at $(x, 1+y, z)$ 2·80 (5) Å, C(33)···H(32) at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ 2·87 (4) Å.

The overlapping of π-electron clouds between neighbouring molecules must have a close relation to the photoconductivity. However, no pair of neighbouring molecules is found, in which the π-electron clouds of pyrazoline overlap.

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3-Ammonio-1,6-anhydro-3-deoxy-β-D-glucopyranose Chloride Monohydrate

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$C_6H_{14}NO_5Cl$, $M_r = 215·6$; orthorhombic, $P2_12_12_1$, $a = 6·2915$ (5), $b = 6·8874$ (8), $c = 21·8987$ (15) Å; $V = 947·6$ Å^3; $Z = 4$; $D_m = 1·510$ g cm^{-3}, $D_x = 1·511$ g cm^{-3}, $R = 0·029$ and $R_w = 0·039$ for 1163 reflections. The $B_{0,3}$ boat conformation deduced from ^{1}H NMR data is not observed. Instead the pyranose ring is a distorted $^1C_4$ chair. The anhydro ring has a $^0T_5$ twist conformation. The hydrogen bonding involves all available (N^+)H and (O)H atoms, the water molecules and the chloride ions, but not the ring oxygens.

Introduction

This work is an extension of the study of the conformation and structural properties of 1,6-anhydro-β-D-glucopyranose and its 3-amino deoxy derivative (Park, Kim & Jeffrey, 1971; Noordik & Jeffrey, 1977). The crystals were provided by Professor M. Cerny, Charles University, Praha, Czechoslovakia, who reported that the 3-amino hydrochloride in solution gave NMR data indicating that the pyranose ring had the $B_{0,3}$ boat conformation (Trnka, Cerny, Budesinsky & Pacek, 1975).

A crystal of dimensions 0·27 × 0·27 × 0·12 mm

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was investigated on a CAD-4 diffractometer to obtain the unit-cell dimensions and to measure all *hkl* and *hkl* diffraction intensities within a range of $2\theta = 150°$. The θ–2θ scan was used with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Absorption corrections were applied with *ABSOR* (Templeton & Templeton, 1973) and $\mu(\text{Cu}\,K\alpha) = 35{\cdot}88\ \text{cm}^{-1}$. The agreement between the symmetry-equivalent intensities was $R = 0{\cdot}033$; these were averaged to give 1163 structure amplitudes of which two had $F^2 < 0$.

The structure was solved directly by the application of *MULTAN* (Germain, Main & Woolfson, 1971) and refined by the full-matrix least-squares program *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962). The H atoms were found on the difference map and refined with isotropic temperature factors. The quantity minimized was $\Sigma w|F_o - kF_c|^2$ with $w^{-1} = \{[\sigma_c^2(F_o^2) + (0{\cdot}04\,F_o^2)^2]/2\}F_o$, where σ_c is from the counting statistics. An isotropic extinction parameter (Coppens & Hamilton, 1970) was included giving a value for $g = 1{\cdot}1\,(1) \times 10^4$. The final $R = \Sigma|F_o - kF_c|/\Sigma|F_o|$, and $R_w = \{\Sigma[w(F_o - kF_c)]^2/\Sigma\, wF_o^2\}^{1/2}$ for 1163 reflections were 0·029 and 0·039 respectively.* The atomic scattering factors used for Cl, O, N and C were those tabulated by Doyle & Turner (1968) and those for H by Stewart, Davidson & Simpson (1965). The atomic parameters are given in Tables 1 and 2. The thermal ellipsoids are shown in Fig. 1. The atomic notation, the bond lengths and the torsion angles for the pyranose and anhydro rings are given in Fig. 2. The bond angles are given in Table 3, together with some vicinal C–H bond torsion angles useful in the interpretation of NMR J_{ij} coupling constants. The

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32342 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^4$) *for nonhydrogen atoms*

The anisotropic thermal parameters are in the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	2193 (1)	6510 (1)	4329 (0)	214 (2)	144 (1)	27 (0)	−11 (1)	13 (0)	−6 (0)
N	5137 (3)	7606 (3)	764 (1)	205 (5)	141 (3)	13 (0)	−14 (4)	7 (1)	6 (1)
C(1)	1295 (4)	5189 (3)	1488 (1)	165 (5)	145 (4)	17 (0)	−29 (4)	0 (1)	1 (1)
C(2)	3409 (3)	4673 (3)	1192 (1)	194 (5)	107 (3)	13 (0)	−17 (4)	3 (1)	−1 (1)
C(3)	5077 (3)	6284 (3)	1306 (1)	154 (4)	112 (4)	12 (0)	−2 (4)	3 (1)	2 (1)
C(4)	4774 (3)	7439 (3)	1906 (1)	181 (5)	129 (4)	13 (0)	−9 (4)	−4 (1)	−3 (1)
C(5)	2456 (4)	7467 (3)	2120 (1)	201 (6)	138 (4)	14 (0)	3 (4)	6 (1)	−4 (1)
C(6)	971 (4)	8474 (4)	1678 (1)	185 (5)	175 (5)	20 (0)	35 (6)	4 (1)	−4 (1)
O(1)	568 (3)	6974 (2)	1230 (1)	182 (4)	167 (4)	20 (0)	10 (3)	−9 (1)	1 (1)
O(2)	4065 (3)	2889 (2)	1458 (1)	277 (5)	113 (3)	19 (0)	19 (4)	15 (1)	4 (1)
O(4)	6089 (3)	6490 (3)	2337 (1)	245 (4)	192 (3)	15 (0)	25 (5)	−18 (1)	−6 (1)
O(5)	1635 (3)	5524 (2)	2117 (1)	223 (4)	156 (3)	15 (0)	−23 (4)	14 (1)	6 (1)
O(*W*)	6947 (3)	5210 (3)	−147 (1)	241 (4)	173 (3)	17 (0)	−18 (4)	−3 (1)	2 (1)

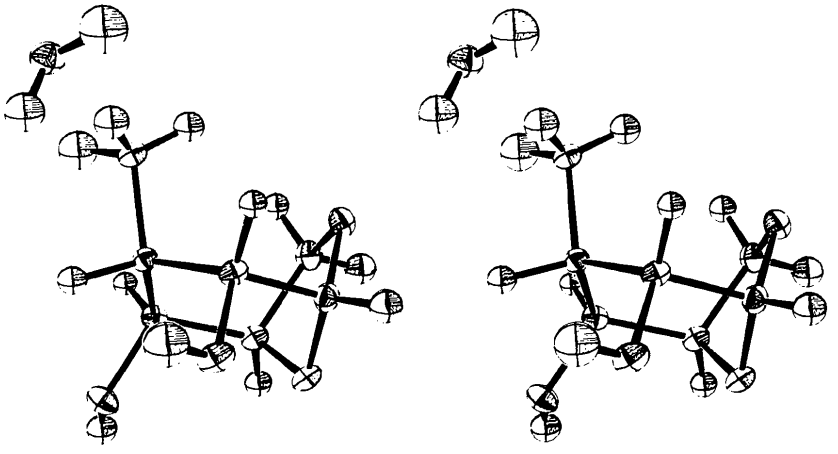

Fig. 1. The thermal ellipsoids at 20% probability of the ammonio-1,6-anhydro-β-D-glucopyranose ion and the water molecule in the chloride monohydrate (Johnson, 1976).

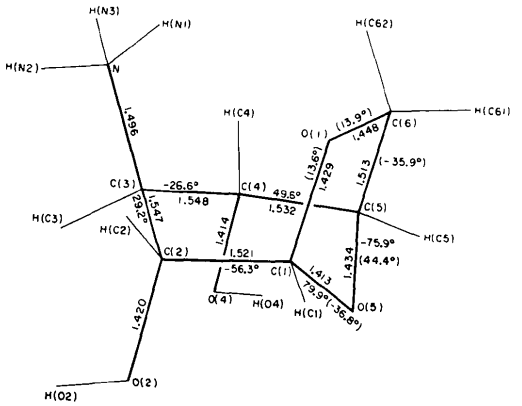

Fig. 2. The atomic notation, C–C, C–N and C–O bond lengths (Å) and ring torsion angles (°) (those for the anhydro ring are in parentheses).

Table 2. *Fractional atomic coordinates* (×10^3), *isotropic thermal parameters* (Å^2) *and bond distances* (Å) *for the hydrogen atoms*

	x	y	z	B_{iso}	N,C,O–H
H(N1)	382 (5)	816 (5)	66 (1)	3·6 (6)	0·94 (3)
H(N2)	563 (5)	692 (5)	46 (1)	4·2 (6)	0·88 (3)
H(N3)	625 (6)	875 (6)	85 (2)	6·0 (8)	1·07 (4)
H(O2)	510 (8)	240 (6)	127 (2)	6·2 (9)	0·85 (5)
H(O4)	610 (5)	713 (5)	267 (1)	3·8 (6)	0·86 (3)
H(C1)	27 (5)	419 (5)	142 (1)	3·9 (6)	0·96 (3)
H(C2)	303 (4)	455 (4)	74 (1)	2·5 (4)	1·03 (2)
H(C3)	668 (4)	560 (4)	131 (1)	2·9 (5)	1·11 (3)
H(C4)	530 (4)	878 (4)	184 (1)	2·3 (5)	0·99 (3)
H(C5)	229 (4)	789 (4)	255 (1)	3·2 (5)	1·00 (3)
H(C61)	−38 (5)	883 (5)	186 (1)	4·5 (7)	0·97 (3)
H(C62)	155 (5)	962 (4)	145 (1)	3·2 (5)	1·00 (3)
H(O*W*1)	747 (5)	416 (5)	5 (1)	4·4 (6)	0·91 (3)
H(O*W*2)	590 (7)	464 (6)	−35 (1)	6·6 (9)	0·89 (4)

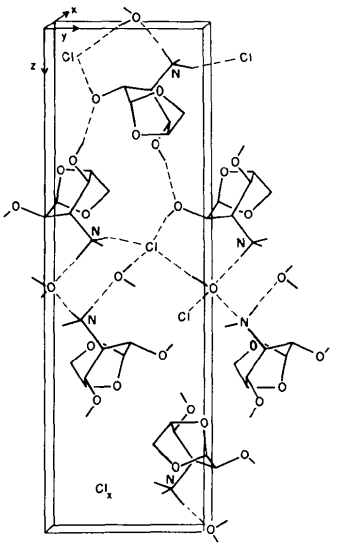

Fig. 3. Unit-cell contents and molecular packing of 3-ammonio-1,6-anhydro-β-D-glucopyranose chloride monohydrate. Dashed lines represent hydrogen bonds.

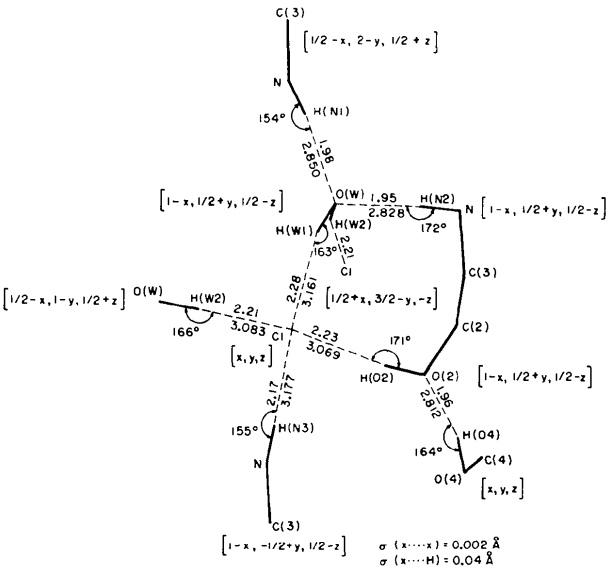

Fig. 4. The hydrogen-bonding geometry in 3-ammonio-1,6-anhydro-β-D-glucopyranose chloride monohydrate. Dashed lines represent hydrogen bonds; the shorter distances are those from the hydrogen atoms.

Table 3. *The valence bond angles* (°) *and some vicinal* C–H *bond torsional angles* (°)

C(2)–C(1)–O(1)	108·2 (2)	C(2)–C(3)–C(4)	114·9 (2)	C(4)–C(5)–C(6)	113·5 (2)
C(2)–C(1)–O(5)	108·7 (2)	C(2)–C(3)–N	109·0 (1)	C(4)–C(5)–O(5)	109·2 (2)
O(1)–C(1)–O(5)	107·1 (2)	N–C(3)–C(4)	111·3 (2)	O(5)–C(5)–C(6)	101·7 (2)
C(1)–C(2)–C(3)	110·9 (2)	C(3)–C(4)–C(5)	112·5 (2)	C(5)–C(6)–O(1)	102·4 (2)
C(1)–C(2)–O(2)	106·4 (2)	C(3)–C(4)–O(4)	104·8 (2)	C(6)–O(1)–C(1)	106·8 (2)
O(2)–C(2)–C(3)	110·9 (2)	O(4)–C(4)–C(5)	111·1 (2)	C(5)–O(5)–C(1)	102·2 (1)

H(C1)–C(1)–C(2)–H(C2)	60·2	H(C3)–C(3)–C(4)–H(C4)	89·2	H(C5)–C(5)–C(6)–H(C61)	−31·3
H(C2)–C(2)–C(3)–H(C3)	−94·4	H(C4)–C(4)–C(5)–H(C5)	−73·7	H(C5)–C(5)–C(6)–H(C62)	96·3

molecular arrangement in the unit cell is shown in Fig 3 and the hydrogen-bonding geometry in Fig. 4.

Discussion

The dimensions of the 3-ammonio cation are very similar to those of the neutral amine molecule (Noordik & Jeffrey, 1977). The glucopyranose ring is distorted from the regular $^1C_4$ chair, being flatter at C(3) and sharper at O(5). The ring conformation is midway between that of the chair and the sofa in which C(3) would be in the same plane as the other four C atoms of the pyranose ring.

The ring-puckering parameters for the pyranose ring, calculated by the method of Cremer & Pople (1975), are $\theta = 147{\cdot}6$ (152·6), $\phi = 173{\cdot}8°$ (179·6), $q_2 = 0{\cdot}330$ (0·283), $q_3 = -0{\cdot}520$ (−0·546) and $Q = 0{\cdot}616$ Å (0·615). The corresponding values for the 3-amino molecule are given in parentheses. The total puckering is the same, but the distortion is slightly more towards the sofa conformation ($\theta = 90°$) and has a larger twist-boat component ($\phi = 90°$). The anhydro ring has puckering parameters $\phi = 19{\cdot}7°$ and $q_2 = 0{\cdot}413$ Å. In terms of the pseudorotational phase angle of Altona & Sundaralingam (1972), P is 1° from that of the symmetrical O(5) twist conformation.

A comparison of the ring torsion angles given in Fig. 2, with those of the neutral 3-amino compound and other 1,6-anhydro-β-D-pyranose molecules, given in Table 2 of Noordik & Jeffrey (1977), shows that this molecule is the most distorted of the series of six related structures which have been studied in the crystalline state. The ring torsion angles about the C(2)—C(3) and C(3)—C(4) bonds are the smallest, 29 and −27°, and that about O(1)—C(6) of the anhydro ring is the largest, 14°. The pyranose ring is the least symmetrical about the C(3)···O(5) diagonal, with greater differences between the pairs of C—C—O—C and C—C—C—O torsion angles than in the other molecules.

Despite this evidence of additional strain in the fused-ring system, the molecule does not change over into the more strain-free $B_{0,3}$ boat conformation in which C(3) lies on the opposite side of the C(1), C(2), C(4), C(5) plane to the anhydro ring.

The ^{1}H NMR studies of this and the corresponding 3-amino compound, by Trnka, Cerny, Budesinsky & Pacek (1975), which prompted this investigation, provide strong evidence that, when dissolved in hexadeuterodimethyl sulfoxide, this transformation to the boat conformation does take place. The transformation in solution from the $^1C_4$ chair to a 45 : 50 $^1C_4 \rightleftharpoons B_{0,3}$ equilibrium and to a predominantly $B_{0,3}$ conformation, as the substitution on C(3) changes from —OH to NH_2 and NH_3^+, corresponds in the solid state to increased flattening of the $^1C_4$ chair at C(3) and increased twist in the anhydro ring. We find it difficult to believe that it is the intermolecular and interionic hydrogen bonding which stabilizes these distorted chair conformations in the crystals; the hydrogen bonding is very different in the neutral amine and the hydrated ammonium salt. We therefore favor the alternative explanation that the difference between the solid and solution conformations is a consequence of the effect of the dimethyl sulfoxide solvent on the relative importance of the competing intramolecular interactions. The conformational equilibrium will be especially sensitive to those interactions involving the shorter separations, *i.e.* O(2)H···O(4)H, where an intramolecular hydrogen bond is possible and O(3)H, N(3)H or N^+(3)H···HC(1) in the chair form *versus* the important C(3)H···O(5) interaction in the boat conformation. This question is discussed in more detail by Trnka, Cerny, Budesinsky & Pacek (1975).

The bond lengths and valence angles in this structure agree well with those observed in the neutron diffraction study of the 3-amino compound (Noordik & Jeffrey, 1977). The C(3)—C(2) and C(3)—C(4) bonds are longer than the other two C—C bonds in the pyranose ring by about 0·02 Å, as in the neutral molecule, and the C(5)—O(5)—C(1)—O(1)—C(6) bond sequence shows a similar distribution of two short bonds, 1·413, 1·429 Å, flanked by two long bonds 1·434 and 1·448 Å (*cf.* Table 3 of Noordik & Jeffrey, 1977). The C—N^+ bond length of 1·496 Å is longer than the C—N bond, 1·470 Å. The bond angles, which range between 102 and 114°, show a remarkable correspondence between the two molecules, with differences of less than 2°, except for C(3)—C(2)—O(2), C(3)—C(4)—O(4), and C(4)—C(3)—N.

The hydrogen bonding is shown schematically below and in Figs. 3 and 4. Both the water molecules and the chloride ions are four coordinated, that of the water being approximately tetrahedral with H—O—H angles between 99 and 121°.

```
        N+—H(1)          H—O(W)
           ⋮                ⋮
Cl−···H—O(W)—H···Cl−···H—O(2)···H—O(4)
           ⋮                ⋮
        N+—H(2)      N+—H(3)
```

The N^+H_3 group forms two strong bonds to the water molecules with H—O distances of 1·98 and 1·95 Å. The water molecules provide two of the four hydrogen bonds to the chloride ions. The other two bonds are from N^+—H and O—H, to form an irregular four-coordination with H—Cl—H angles between 78 and 163°. The N^+H···Cl^- bond is slightly shorter by 0·07 Å than the O—H···Cl^- bonds.

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Structure Cristalline et Moléculaire d'un Nouvel Alcaloïde Bisindolique: Complexe Moléculaire 1:2 Strychnofoline–Ethanol ($C_{30}H_{34}N_4O_2.2C_2H_6O$)

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(*Reçu le* 27 *octobre* 1976, *accepté le* 24 *novembre* 1976)

Strychnofoline is a phenolic alkaloid isolated from leaves of *Strychnos usambarensis*. The crystals of $C_{30}H_{34}N_4O_2.2C_2H_6O$ are monoclinic, space group $P2_1$, with $a = 9{\cdot}019$ (3), $b = 17{\cdot}941$ (5), $c = 10{\cdot}598$ (3) Å and $\beta = 99{\cdot}69$ (3)°, $Z = 2$. The crystal structure has been solved by direct methods, and refined with a block-diagonal least-squares method to a final R value of 7·3% (2820 reflexions). The configuration determined by biogenetic arguments is 3*S*,4*R*,7*S*,15*S*,17*S*,20*R*. This is the first oxindole found in a strychnos.

Introduction

La strychnofoline ($C_{30}H_{34}N_4O_2$) est un alcaloïde phénolique extrait des feuilles du *Strychnos usambarensis* (Loganiaceae). A l'aide des spectres (masse, UV, IR et RMN), la détermination de la structure moléculaire s'est avérée hasardeuse. Nous avons jugé intéressant d'entreprendre cette étude, afin de résoudre ce problème. D'autre part, nous proposons une configuration absolue à partir d'arguments biogénétiques.

Partie expérimentale

Les cristaux ont été obtenus par évaporation lente d'une solution éthanolique. Lors de la détermination de la structure, il est apparu dans la maille unité quatre molécules de solvant. L'échantillon retenu pour l'étude mesurait 0,3 × 0,3 × 0,35 mm. Les données cristallographiques sont reprises dans le Tableau 1. Les intensités ont été collectées au moyen d'un diffractomètre à quatre cercles Hilger & Watts. Parmi les 3040 réflex-