Acta Chemica Scandinavica B 39 (1985) 705–716

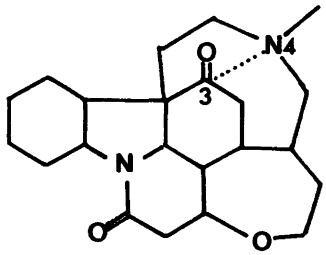
Structural Study of the Strychnine Molecule in Crystals of the Free Base and of the Nitric Acid Complex

ARVID MOSTAD

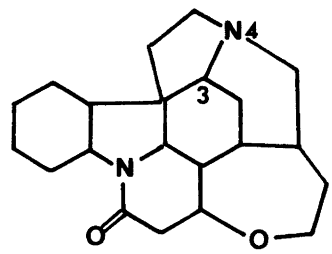
Department of Chemistry, University of Oslo, 0315 Oslo 3, Norway

The crystal and molecular structure of strychnine as free base, as well as in the form of its nitric acid salt, has been determined by X-ray crystallographic methods at temperatures of about 133 K. Both crystals are orthorhombic, space group $P2_12_12_1$ and the structure determinations were based on the measurements of 2427 and 2339 reflections, respectively. Cell dimensions for the free base are a=11.321(2) Å, b=11.810(3) Å and c=12.016(3) Å, whereas those for the nitrate are a=7.411(2) Å, b=8.058(3) Å and c=30.743(10) Å. The structures were refined to conventional R-factors of 0.033 and 0.045, respectively. Estimated standard deviations in both structure determinations are about $2-4 \cdot 10^{-3}$ Å in interatomic distances, and 0.1–0.3° in angles when hydrogen atoms are not involved. Differences in bond lengths involving the N4 atom as displayed by the two structures are discussed.

Previous X-ray crystallographic studies of some Strychnos alkaloids where the N4 nitrogen atom is not formally bonded to the C3 atom, have proved the existence of a strong transannular interaction between these atoms in several compounds.[1-3] (see icajine below). It is of interest to compare these nonbonded distances with the N4–C3 distance in compounds such as strychnine, where a formal N4–C3 bond is established.



ICAJINE



STRYCHNINE

However, the earlier reports on the structure of strychnine[4-6] do not give the bond lengths and angles with the necessary accuracy, and since it was also of interest to study the influence of quaternisation of the N4 atom on the nearest molecular environment of that atom, the crystal structures of strychnine as a free base, as well as of the nitric acid salt have been studied.

0302-4369/85 $2.50

Table 1. Experimental conditions for strychnine.

	Free base	Nitrate
Instrument	SYNTEX $P\bar{1}$	
Radiation	Graphite crystal monochromated Mo$K\alpha$, λ=0.71067 Å	
Crystal dimensions/mm	0.3×0.3×0.6	0.4×0.4×0.2
Scanning mode	$\theta/2\theta$	ω
Scan speed/° mm^{-1}	3.0 (2θ)	3.0 (ω)
Scan range	$2\theta_{\alpha 1}-1.0$ to $2\theta_{\alpha 2}+1.2$	1.0
Back ground counts	For 0.35 of scan time at scan limits	
Temperature/K[a]	133	133
2θ range	2.0–60.0	2.0–60.0
Number of reflections	2683	3116
Number of reflections with $I>2.5\sigma(I)$	2427	2339
Number of standard reflections	3	3
Number of reflections between standard reflections	57	57

[a] Temperature measured at crystal site.

EXPERIMENTAL

Strychnine nitrate was found to exist as large colourless rhombohedral prismatic crystals that could be used directly for the X-ray experiments, whereas the free base had to be recrystallized from a mixture of acetone and chloroform from which well-formed crystals separated by evaporation. Cell parameters in both structures were determined by a least squares fit to the diffractometer settings for 15 general reflections. The standard deviation for the intensities were calculated from $\sigma(I)=|C_T+(0.002\ C_N)^2|^{\frac{1}{2}}$, where C_T is the total number of counts, and C_N is the scan count minus background count. The usual corrections were made for Lorentz and polarization effects, whereas no corrections were made for absorption or extinction. Scattering factors used were those of Doyle and Turner for O, N and C,[7] and of Stewart, Davidson and Simpson for H.[8] Description of the computer programs applied is given in Ref. 9.

The quality minimized in the least-squares calculation was $\Sigma w(\Delta F),^2$ where w is the inverse of the variance of the observed structure factors.

The remaining experimental conditions are given in Table 1.

CRYSTAL DATA

Strychnine. $C_{21}O_2N_2H_{22}$, orthorhombic, a=11.321(2) Å, b=11.810(3) Å, c=12.016(3) Å, V=1611.6 Å^3, M=334.2, Z=4, $F(000)$=712, Space group $P2_12_12_1$ (No. 19).

Strychnine nitrate. $C_{21}O_2N_2H_{23}{}^+NO_3^-$, orthorhombic, a=7.411(2) Å, b=8.058(3) Å, c=30.743(10) Å, V=1836.0 Å^3, M=397.3, Z=4, $F(000)$=840, Space group $P2_12_12_1$ (No. 19).

STRUCTURE DETERMINATION

The structure of strychnine nitrate was solved by direct methods using the program assembly MULTAN,[10] and the positions of the non hydrogen atoms refined by Fourier methods. Hydrogen atomic positional parameters were calculated from stereochemical considera-

Table 2. Fractional atomic coordinates in the crystals of strychnine. Estimated standard deviations in parentheses.

Atom	*X*	*Y*	*Z*
O17	−0.0382(1)	0.4861(1)	0.4998(1)
O23	0.3690(1)	0.4909(1)	0.4164(1)
N1	0.2246(1)	0.5837(1)	0.3202(1)
N4	−0.1050(1)	0.7934(1)	0.2327(1)
C2	0.1002(1)	0.6257(1)	0.3248(1)
C3	0.0162(1)	0.8240(1)	0.2708(1)
C5	−0.0969(1)	0.6904(1)	0.1630(1)
C6	0.0330(1)	0.6847(1)	0.1297(1)
C7	0.0959(1)	0.7232(1)	0.2373(1)
C8	0.2248(1)	0.7488(1)	0.2185(1)
C9	0.2751(1)	0.8380(1)	0.1601(1)
C10	0.3982(2)	0.8403(2)	0.1452(1)
C11	0.4671(2)	0.7525(2)	0.1864(1)
C12	0.4183(1)	0.6619(2)	0.2457(1)
C13	0.2960(1)	0.6627(1)	0.2622(1)
C14	0.0189(1)	0.8521(1)	0.3944(1)
C15	−0.0212(1)	0.7472(1)	0.4598(1)
C16	0.0773(1)	0.6584(1)	0.4467(1)
C17	0.0694(1)	0.5482(1)	0.5147(1)
C18	−0.1417(1)	0.5423(1)	0.5426(1)
C19	−0.1963(1)	0.6180(1)	0.4562(1)
C20	−0.1422(1)	0.7098(1)	0.4175(1)
C21	−0.1908(1)	0.7822(1)	0.3243(1)
C22	0.1680(1)	0.4661(1)	0.4781(1)
C23	0.2641(1)	0.5140(1)	0.4043(1)
H2	0.044(2)	0.566(2)	0.304(1)
H3	0.043(2)	0.890(2)	0.226(2)
H51	−0.148(2)	0.696(2)	0.098(2)
H52	−0.122(2)	0.624(2)	0.208(2)
H61	0.051(2)	0.738(1)	0.069(1)
H62	0.062(2)	0.610(2)	0.105(2)
H9	0.223(2)	0.900(2)	0.128(2)
H10	0.434(2)	0.904(2)	0.102(2)
H11	0.553(2)	0.751(2)	0.174(2)
H12	0.467(2)	0.600(2)	0.273(2)
H141	−0.034(2)	0.915(2)	0.411(2)
H142	0.099(2)	0.874(2)	0.411(2)
H15	−0.029(2)	0.768(2)	0.541(2)
H16	0.148(2)	0.699(2)	0.473(2)
H17	0.076(2)	0.564(1)	0.595(2)
H181	−0.120(2)	0.582(2)	0.614(2)
H182	−0.195(2)	0.481(2)	0.564(2)
H19	−0.271(2)	0.599(2)	0.426(2)
H211	−0.210(2)	0.859(2)	0.353(2)
H212	−0.262(2)	0.748(2)	0.291(2)
H221	0.127(2)	0.405(2)	0.437(2)
H222	0.202(2)	0.430(2)	0.544(2)

Table 3. Fractional atomic coordinates in the crystals of strychnine nitrate. Estimated standard deviations in parentheses.

Atom	*X*	*Y*	*Z*
O1	0.6990(3)	0.0943(2)	0.7805(1)
O2	0.8784(3)	0.3070(2)	0.7772(1)
O3	0.9351(3)	0.1067(3)	0.8223(1)
O17	0.5052(3)	−0.7686(2)	0.8697(1)
O23	0.9436(3)	−0.7326(2)	0.9797(1)
NO	0.8403(4)	0.1710(3)	0.7935(1)
N1	0.9182(3)	−0.5581(3)	0.9213(1)
N4	0.6749(3)	−0.2072(3)	0.8169(1)
C2	0.7905(4)	−0.4980(3)	0.8869(1)
C3	0.7158(3)	−0.1923(3)	0.8658(1)
C5	0.8191(4)	−0.3165(3)	0.7969(1)
C6	0.9672(4)	−0.3246(3)	0.8308(1)
C7	0.8636(3)	−0.3218(3)	0.8747(1)
C8	0.9866(3)	−0.2813(3)	0.9127(1)
C9	1.0685(4)	−0.1320(3)	0.9232(1)
C10	1.1870(4)	−0.1272(4)	0.9590(1)
C11	1.2255(4)	−0.2712(4)	0.9817(1)
C12	1.1457(4)	−0.4228(4)	0.9713(1)
C13	1.0209(4)	−0.4236(3)	0.9370(1)
C14	0.5435(3)	−0.2107(3)	0.8920(1)
C15	0.4688(4)	−0.3852(3)	0.8846(1)
C16	0.6015(4)	−0.5066(3)	0.9067(1)
C17	0.5496(4)	−0.6900(3)	0.9102(1)
C18	0.3463(4)	−0.7070(4)	0.8483(1)
C19	0.3881(4)	−0.5600(3)	0.8200(1)
C20	0.4448(3)	−0.4164(3)	0.8359(1)
C21	0.4865(3)	−0.2689(3)	0.8075(1)
C22	0.7121(4)	−0.7900(4)	0.9266(1)
C23	0.8664(4)	−0.6928(3)	0.9462(1)
H2	0.804(3)	−0.568(3)	0.862(1)
H3	0.773(3)	−0.077(3)	0.870(1)
H51	0.857(4)	−0.267(3)	0.767(1)
H52	0.768(4)	−0.435(4)	0.794(1)
H61	1.050(3)	−0.431(3)	0.829(1)
H62	1.036(4)	−0.232(4)	0.829(1)
H9	1.044(4)	−0.035(3)	0.905(1)
H10	1.251(4)	−0.028(4)	0.965(1)
H11	1.312(4)	−0.271(4)	1.006(1)
H12	1.169(4)	−0.526(4)	0.987(1)
H141	0.452(4)	−0.129(3)	0.884(1)
H142	0.577(4)	−0.193(3)	0.924(1)
H15	0.354(4)	−0.398(4)	0.898(1)
H16	0.615(4)	−0.459(3)	0.938(1)
H17	0.452(4)	−0.703(4)	0.931(1)
H181	0.253(4)	−0.687(4)	0.866(1)
H182	0.298(4)	−0.805(4)	0.830(1)
H19	0.370(3)	−0.577(3)	0.790(1)
H211	0.401(4)	−0.169(3)	0.813(1)
H212	0.486(4)	−0.300(3)	0.776(1)
H221	0.778(5)	−0.844(5)	−0.899(1)
H222	0.670(4)	−0.870(4)	0.946(1)
HN4	0.689(4)	−0.093(4)	0.804(1)

tions, and the final refinement by least-squares calculations included positional parameters for all atoms, anisotropic thermal parameters for the heavier atoms and isotropic thermal parameters for hydrogen atoms. The final statistical parameters were $R=0.045$, $R_w=0.040$ and $S-[w(\Delta F)^2/(n-m)]^{\frac{1}{2}}=1.6$.

The structure of strychnine in the free base form was also solved by direct methods, this time by the use of the program assembly MITHRIL,[11] which gave the positions of the nonhydrogen atoms. Following a least-squares refinement including isotropic temperature factors, the hydrogen atoms were found from difference Fourier syntheses. Final least-squares refinements of all positional parameters, anisotropic thermal parameters for the non hydrogen atoms, and isotropic temperature factors for the hydrogen atoms converged to a conventional R-factor of 0.033, $R_w=0.037$ and $S=2.3$.

Final parameters are given in Tables 2 and 3 and structural data are listed in Tables 4 and 5. The structure factor listing and thermal parameters may be obtained from the author. Standard deviations given are calculated from the variance-covariance matrix and found to be $2-4\cdot10^{-3}$ Å in interatomic distances and $0.1-0.3°$ in angles when hydrogen atoms are not involved. Bond lengths and angles involving hydrogen atoms have standard deviations $2\cdot10^{-2}$ Å and 2°, respectively.

DESCRIPTION AND DISCUSSION

A drawing of the strychnine molecule as it appears in the crystal of the nitrate is given in Fig. 1 together with the numbering of the atoms. A stereoscopic drawing of the molecule is

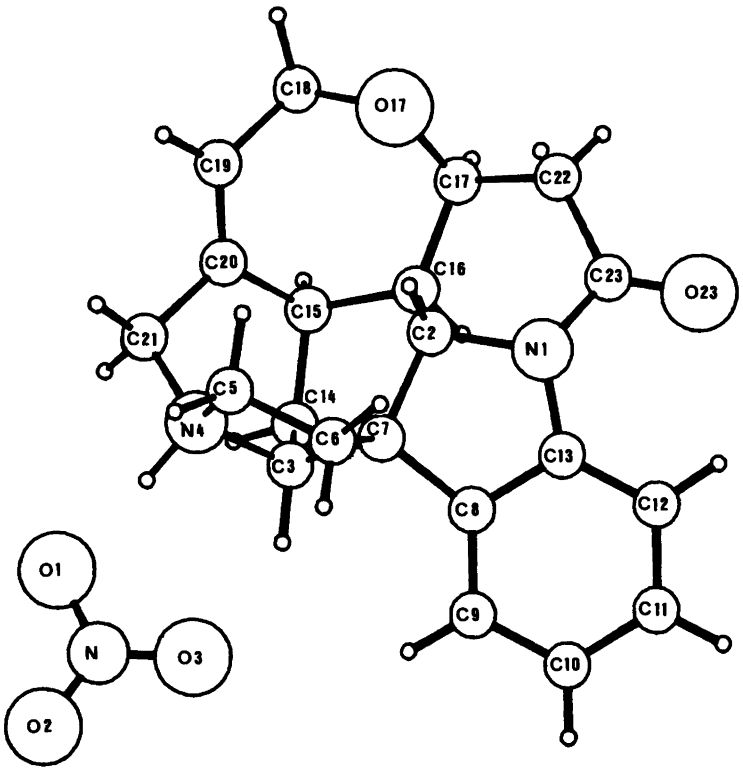


Fig. 1. The strychnine cation as it appears in the crystals of the nitrate.

Table 4. Bond lengths, angles and dihedral angles in strychnine. Estimated standard deviations in parentheses. The C–H distances are all between 0.95(2) and 1.01(2) Å.

Distance	(Å)	Distance	(Å)
O17–C17	1.433(2)	O17–C18	1.442(2)
O23–C23	1.227(2)	N1–C2	1.494(2)
N1–C13	1.417(2)	N1–C23	1.379(2)
N4–C3	1.491(2)	N4–C5	1.480(2)
N4–C21	1.474(2)	C2–C7	1.560(2)
C2–C16	1.538(2)	C3–C7	1.546(2)
C3–C14	1.523(2)	C5–C6	1.525(2)
C6–C7	1.545(2)	C7–C8	1.507(2)
C8–C9	1.388(2)	C8–C13	1.401(2)
C9–C10	1.404(2)	C10–C11	1.388(3)
C11–C12	1.399(3)	C12–C13	1.399(2)
C14–C15	1.536(2)	C15–C16	1.539(2)
C15–C20	1.526(2)	C16–C17	1.538(2)
C17–C22	1.543(2)	C18–C19	1.503(2)
C19–C20	1.330(2)	C20–C21	1.512(2)
C22–C23	1.512(2)		
Angle	**(°)**	**Angle**	**(°)**
C17–O17–C18	114.3(1)	C2–N1–C13	109.7(1)
C2–N1–C23	118.5(1)	C13–N1–C23	124.6(1)
C3–N4–C5	108.4(1)	C3–N4–C21	113.5(1)
C5–N4–C21	113.0(1)	N1–C2–C7	104.5(1)
N1–C2–C16	106.1(1)	C7–C2–C16	116.8(1)
N4–C3–C7	105.7(1)	N4–C3–C14	111.8(1)
C7–C3–C14	114.2(1)	N4–C5–C6	104.1(1)
C5–C6–C7	102.2(1)	C2–C7–C3	114.3(1)
C2–C7–C6	111.2(1)	C2–C7–C8	102.6(1)
C3–C7–C6	100.1(1)	C3–C7–C8	116.7(1)
C6–C7–C8	112.3(1)	C7–C8–C9	128.7(1)
C7–C8–C13	110.8(1)	C9–C8–C13	120.3(1)
C8–C9–C10	119.1(2)	C9–C10–C11	119.8(2)
C10–C11–C12	122.1(2)	C11–C12–C13	117.3(2)
N1–C13–C8	109.5(1)	N1–C13–C12	129.1(1)
C8–C13–C12	121.4(1)	C3–C14–C15	108.5(1)
C14–C15–C16	106.5(1)	C14–C15–C20	109.2(1)
C16–C15–C20	114.8(1)	C2–C16–C15	113.0(1)
C2–C16–C17	107.6(1)	C15–C16–C17	118.7(1)
O17–C17–C16	114.6(1)	O17–C17–C22	104.9(1)
C16–C17–C22	109.8(1)	O17–C18–C19	111.2(1)
C18–C19–C20	122.5(1)	C15–C20–C19	122.2(1)
C15–C20–C21	114.2(1)	C19–C20–C21	123.5(1)
N4–C21–C20	111.3(1)	C17–C22–C23	116.9(1)
O23–C23–N1	122.2(1)	O23–C23–C22	122.9(1)
N1–C23–C22	114.9(1)		
Dihedral angle	**(°)**	**Dihedral angle**	**(°)**
C17–O17–C18–C19	88.8(2)	C14–C3–C7–C6	155.7(1)
C18–O17–C17–C16	−67.0(2)	C14–C3–C7–C8	−82.9(2)
C18–O17–C17–C22	172.5(1)	N4–C5–C6–C7	38.7(1)
C2–N1–C13–C8	−5.9(2)	C5–C6–C7–C2	77.9(1)
C2–N1–C13–C12	174.7(1)	C5–C6–C7–C3	−43.2(1)
C13–N1–C2–C7	14.3(1)	C5–C6–C7–C8	−167.7(1)
C13–N1–C2–C16	−109.8(1)	C2–C7–C8–C6	−170.6(1)

C2–N1–C23–C23	−168.0(1)	C2–C7–C8–C13	14.0(2)
C2–N1–C23–C22	13.5(2)	C3–C7–C8–C9	−44.8(2)
C23–N1–C2–C7	166.1(1)	C3–C7–C8–C13	139.7(1)
C23–N1–C2–C16	42.1(2)	C6–C7–C8–C9	69.9(2)
C13–N1–C23–C23	−20.7(2)	C6–C7–C8–C13	−105.5(1)
C13–N1–C23–C22	160.9(1)	C7–C8–C9–C10	−174.7(2)
C23–N1–C13–C8	−155.6(1)	C7–C8–C13–N1	−5.7(2)
C23–N1–C13–C12	25.0(2)	C7–C8–C13–C12	173.8(1)
C3–N4–C5–C6	−18.4(2)	C3–C14–C15–C16	69.2(2)
C5–N2–C3–C7	−9.3(1)	C3–C14–C15–C20	−55.3(2)
C5–N4–C3–C14	−134.1(1)	C14–C15–C16–C2	−59.7(2)
C3–N4–C21–C20	−48.2(2)	C14–C15–C16–C17	172.9(1)
C21–N4–C3–C7	117.1(1)	C14–C15–C20–C19	177.2(1)
C21–N4–C3–C14	−7.7(2)	C14–C15–C20–C21	.4(2)
C5–N4–C21–C20	75.8(2)	C16–C15–C20–C19	57.8(2)
C21–N4–C5–C6	−145.1(1)	C16–C15–C20–C21	−119.0(1)
N1–C2–C7–C3	−143.8(1)	C20–C15–C16–C2	61.2(2)
N1–C2–C7–C6	103.8(1)	C20–C15–C16–C17	−66.2(2)
N1–C2–C7–C8	−16.4(1)	C2–C16–C17–C17	−74.6(1)
N1–C2–C15–C15	155.5(1)	C2–C16–C17–C22	43.2(2)
N1–C2–C16–C17	−71.5(1)	C15–C16–C17–C17	55.3(2)
C7–C2–C16–C15	39.5(2)	C15–C16–C17–C22	173.1(1)
C7–C2–C16–C17	172.6(1)	O17–C17–C22–C23	135.3(1)
C16–C2–C7–C3	−26.9(2)	C16–C17–C22–C23	11.7(2)
C16–C2–C7–C6	−139.3(1)	O17–C18–C19–C20	−66.0(2)
C16–C2–C7–C8	100.4(1)	C18–C19–C20–C15	−1.5(2)
N4–C3–C7–C2	−86.4(1)	C18–C19–C20–C21	175.0(1)
N4–C3–C7–C6	32.4(1)	C15–C20–C21–N4	52.5(2)
N4–C3–C7–C8	153.9(1)	C19–C20–C21–N4	−124.3(2)
N4–C3–C14–C15	60.9(2)	C17–C22–C23–O23	138.5(2)
C7–C3–C14–C15	−59.0(2)	C17–C22–C23–N1	−43.0(2)
C14–C3–C7–C2	36.9(2)		

shown in Fig. 2. The molecular packing in the crystals of strychnine nitrate is illustrated in Fig. 3. There is a strong hydrogen bond between N4 in the cationic strychnine molecule and O1 in the nitrate ion. The bond is almost linear, the O1–H–N4 angle being 175.4°, the distances O1–H and O1–N4 is 1.68 and 2.680 Å, respectively, and the angle NO–O1–H is 109.5°. Except for this bond, the shortest contact between the two ions is between O3 in the nitrate ion and H3 in strychnine, the O3–H3 distance being 2.40 Å and O3–C3 3.199 Å.

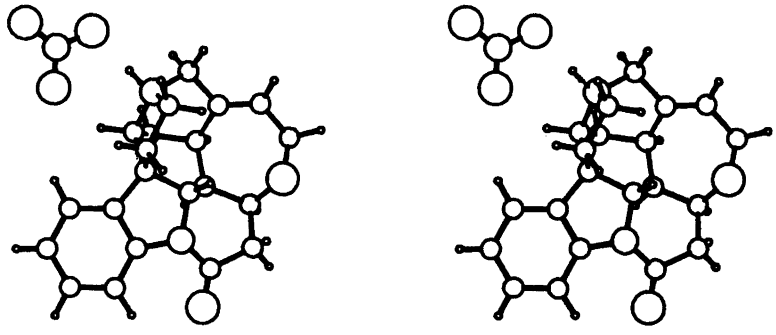


Fig. 2. Stereoscopic drawing of the strychnine nitrate complex.

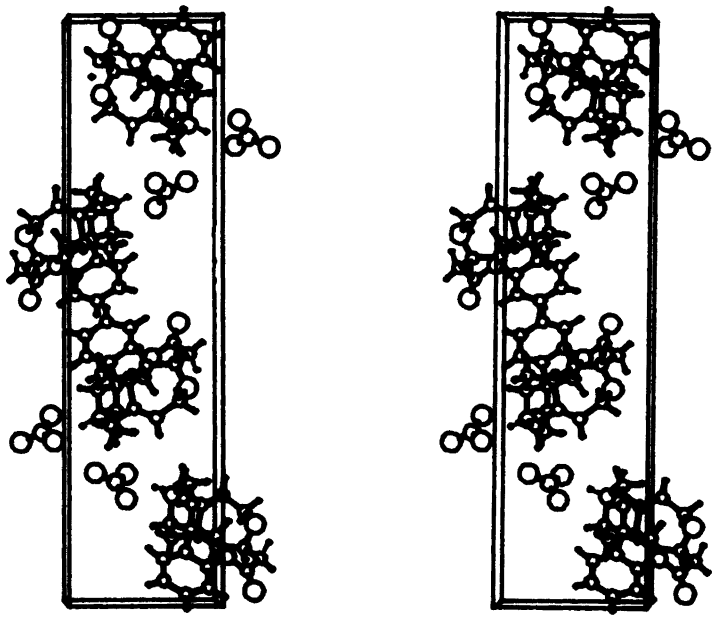


Fig. 3. Molecular packing in the crystals of strychnine nitrate.

Between the units composed of the strychnine$^+$-nitrate$^-$ complex there seem to be only weak van der Waals forces, mostly between carbon atoms connected to N4 and oxygen atoms of the nitrate ion. Thus O1–C21 ($1-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$): 3.228 Å (O1–H212=2.366 Å) O1–C19 ($\frac{1}{2}-x$, $y-\frac{1}{2}$, $1\frac{1}{2}-z$): 3.392 Å (O1–H19=2.607 Å), O2–C5 ($x,y+1,z$): 3.125 Å (O2–H52=2.293 Å), O2–C5 ($2-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$)= 3.347 (O2–H51=2.469) and O3–C22($x,1+y,z$)=3.704 (O2–H221=2.652 Å). There may also be weak interactions between the sp^2 hybridized C19 atom and H61 (x-1,y,z) (2.726 Å) C12–H15 ($1+x,y,z$)=2.748 Å, C13–H15=2.758 and finally between the aromatic groups in molecules

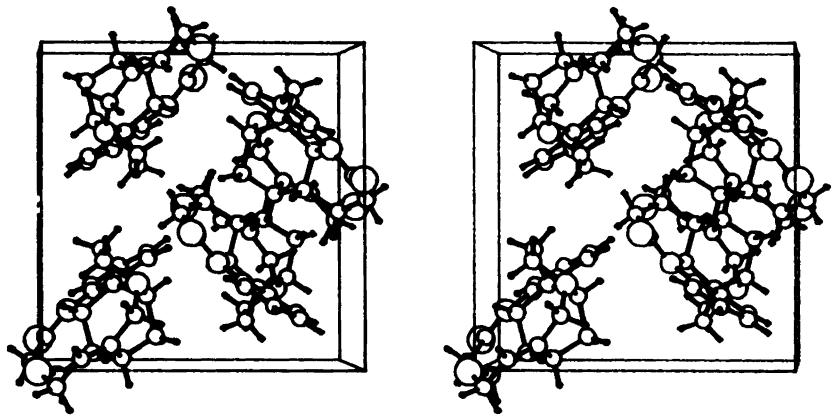


Fig. 4. Molecular packing in the crystals of strychnine.

Table 5. Bond lengths, angles and dihedral angles in strychnine nitrate. Estimated standard deviations in parentheses. The C–H distances are all between 0.90(3) and 1.08(4) Å.

Distance	(Å)	Distance	(Å)
O1–NO	1.279(3)	O2–O2–NO	1.238(3)
O3–NO	1.243(3)	O17–C17	1.436(3)
O17–C18	1.328(3)	O23–C23	1.222(3)
N1–C2	1.500(3)	N1–C13	1.409(3)
N1–C23	1.382(3)	N4–C3	1.538(3)
N4–C5	1.515(3)	N4–C21	1.510(3)
C2–7	1.565(4)	C2–C16	1.529(4)
C3–C7	1.537(3)	C3–C14	1.517(3)
C5–C6	1.515(3)	C6–C7	1.552(3)
C7–C8	1.518(3)	C8–C9	1.386(4)
C8–C13	1.392(3)	C9–C10	1.409(4)
C10–C11	1.383(4)	C11–C12	1.394(4)
C12–C13	1.402(3)	C14–C15	1.528(4)
C15–C16	1.544(4)	C15–C20	1.528(3)
C16–C17	1.532(4)	C17–C22	1.534(4)
C18–C19	1.502(4)	C19–C20	1.325(3)
C20–C21	1.507(3)	C22–C23	1.511(4)
Angle	**(°)**	**Angle**	**(°)**
C17–O17–18	115.6(2)	O1–NO–O2	119.2(3)
O1–NO–O3	118.9(2)	O2–NO–O3	121.9(3)
C2–N1–C13	109.5(2)	C2–N1–C23	117.9(2)
C13–N1–C23	124.4(2)	C3–N4–C5	107.6(2)
C3–N4–C21	113.3(2)	C5–N4–C21	112.5(2)
CN1–CC2–C7	104.1(2)	n1–C2–C16	106.4(2)
C7–C2–C16	116.9(2)	N4–C3–C7	105.2(2)
CN4–C3–C14	110.2(2)	C7–C3–C14	116.0(2)
N4–C5–C6	104.9(2)	C5–C6–C7	103.8(2)
C2–C7–C3	114.3(2)	C2–C7–C6	111.5(2)
C2–C7–C8	102.6(2)	C3–C7–C6	102.0(2)
C3–C7–C8	114.8(2)	C6–C7–C8	112.0(2)
C7–C8–C19	129.0(2)	C7–C8–C13	110.2(2)
C9–C8–C13	120.7(2)	C8–C9–C10	118.6(2)
C9–C10–C11	120.0(3)	C10–C11–C12	122.1(2)
C11–C12–C13	117.1(3)	N1–C1–13–C8	110.5(2)
N1–C13–C12	128.1(2)	C8–C13–C12	121.3(2)
C3–C14–C15	108.4(2)	C14–C15–C16	106.6(2)
C14–C15–C20	109.9(2)	c16–C15–C20	113.6(2)
C2–C16–C15	112.4(2)	C2–C16–C17	107.6(2)
C15–C16–C17	118.9(2)	O17–C17–C16	114.9(2)
O17–C17–C22	103.5(2)	C16–C17–C22	109.5(2)
O17–C18–C19	111.6(2)	C18–C19–C20	122.7(2)
C15–C20–C19	122.8(2)	C15–C20–C21	114.5(2)
C19–C20–C21	122.7(2)	N4–C21–C20	109.8(2)
C17–C22–C23	116.9(2)	O23–C23–N1	122.9(3)
O23–C23–C22	123.6(3)	N1–C23–C22	113.4(2)
Dihedral angle	**(°)**	**Dihedral angle**	**(°)**
C17–O17–C18–C19	86.5(5)	C14–C3–C7–C6	153.3(2)
C18–O17–C17–C16	−65.3(3)	C14–C3–C7–C8	−85.3(3)
C18–O17–C17–C22	175.5(2)	N4–C5–C6–C5	34.7(2)
C2–N1–C13–C8	−6.4(3)	C5–C6–C7–C2	81.5(2)
C2–N1–C13–C12	174.9(2)	C5–C6–C7–C3	−41.0(2)

C13–N1–C2–C7	14.8(2)	C5–C6–C7–C8	−164.2(2)
C13–N1–C2–C16	−109.3(2)	C2–C7–C8–C9	−169.5(3)
C2–N1–C23–O23	−166.4(2)	C2–C7–C8–C13	14.1(3)
C2–N1–C23–C22	16.6(3)	C3–C7–C8–C9	−44.9(3)
C23–N1–C2–C7	164.8(2)	C3–C7–C8–C13	138.7(2)
C23–N1–C2–C16	40.7(3)	C6–C7–C8–C9	70.8(3)
C13–N1–C23–O23	−21.2(4)	C6–C7–C8–C13	−105.6(2)
C13–N1–C22	161.7(2)	C7–C8–C9–C10	−176.1(2)
C23–N1–C13–C8	−154.1(2)	C7–C8–C13–N1	−5.4(3)
C23–N1–C13–C12	27.3(4)	C7–C8–C13–C12	173.4(2)
C3–N4–C5–C6	−15.0(3)	C9–C8–C13–N1	177.9(2)
C5–N4–C3–C7	−10.7(2)	C3–C14–C15–C16	68.7(2)
C5–N4–C3–C14	−136.4(2)	C3–C14–C15–C20	− 54.9(3)
C3–N4–C21–C20	−46.2(3)	C14–C15–C16–C2	−61.5(3)
C21–N4–C3–C7	114.4(2)	C14–C15–C16–C17	171.6(2)
C21–N4–C3–C14	−11.4(3)	C14–C15–C20–C19	177.5(2)
C5–N4–C21–C20	76.1(2)	C14–C15–C20–C21	−3.9(3)
C21–N4–C5–C6	−140.5(2)	C16–C15–C20–C19	58.2(3)
N1–C2–C7–C3	−141.7(2)	C16–C15–C20–C21	−123.3(2)
N1–C2–C7–C6	103.3(2)	C20–C15–C16–C2	59.7(3)
N1–C2–C7–C8	−16.8(2)	C20–C15–C16–C17	−67.2(3)
N1–C2–C16–C15	155.7(2)	C2–C16–C17–O17	−73.7(3)
N1–C2–C16–C17	−71.6(2)	C2–C16–C17–C22	42.2(3)
C7–C2–C16–C15	39.9(3)	C15–C16–C17–O17	55.4(3)
C7–C2–C16–C17	172.6(2)	C15–C16–C17–C22	171.3(2)
C16–C2–C7–C3	−24.6(3)	O17–C17–C22–C23	137.7(2)
C16–C2–C7–C6	−139.7(2)	C16–C17–C22–C23	14.8(3)
C16–C2–C7–C8	100.3(2)	O17–C18–C19–C20	−65.3(4)
N4–C3–C7–C2	−89.2(2)	C18–C19–C20–C15	−1.5(4)
N4–C3–C7–C6	31.3(2)	C18–C19–C20–C21	−179.9(2)
N4–C3–C7–C8	152.6(2)	C15–C20–C21–N4	55.1(3)
N4–C3–C14–C15	63.4(3)	C19–C20–C21–N4	−126.3(3)
C7–C3–C14–C15	−55.9(3)	C17–C22–C23–O23	135.8(3)
C14–C3–C7–C2	32.8(3)	C17–C22–C23–N1	−47.2(3)

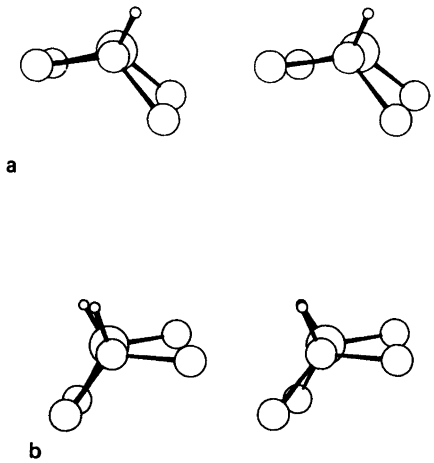


Fig. 5. The conformation about the N4–C bond. A: strychnine, B: strychnine nitrate.

Table 6. Comparison of conformational characteristics of the strychnine molecule as found in the two different crystal structures, given in Å and degrees.

	Strychnine	Strychn. nitr.
The phenyl ring		
C8, C9, C11, C12 planarity	±0.008	±0.003
Distance from plane: C10	0.018	0.025
Distance from plane: C13	0.020	0.038
Angle between planes C13, C8, C9, C10 and C10, C11, C12, C13	1.8	3.0
The pyrrole ring		
C8, C13, C7, N1 planarity	±0.030	±0.030
Distance from plane C2	0.254	0.265
Angle between phenyl and pyrrole planes	3.8	3.9
The 2-oxo-piperidine ring	Twisted boat	
Distance from plane C16, C17, C23 to C22	0.155	0.195
N1	0.628	0.652
C2	1.111	1.115
The piperidine ring	Boat	
C4, C3, C15, C20 planarity	±0.022	±0.047
Distance from plane to C14	0.710	0.718
C21	0.613	0.610
The cyclohexane ring	Chair	
C2, C3, C14, C16 planarity	±0.066	±0.051
Distance from plane to C7	0.401	0.361
C15	−0.775	−0.780
The pyrrolidine ring	Envelope	
N4, C5, C6, C3 planarity	±0.100	±0.090
Distance from plane to C7	0.619	0.576
The oxacycloheptane ring		
Distance from plane C16, C18, C19 to C15	0.967	0.985
C20	0.420	0.424
C17	−0.385	−0.378
O17	−0.935	−0.910
Distance from plane C13, C2, C23 to N1	0.221	0.021
Distance from plane N1, O23, C22 to C23	0.011	0.021
Distance from plane C3, C5, C21 to N4	0.438	0.463
Distance from plane c15, C19, C21 to C20	0.024	0.011

related by screw axes parallel to the x-direction. The C11 atom in one group is pointing towards the C8–C13 bond in the next and the C8–H11 and C13–H11 are 2.850 and 2.820 Å, respectively. The angle between the two aromatic planes is about 83°.

The molecular packing in the crystals of the free base is shown in Fig. 4. From this it may be seen that the O23 atom is central in the interactions between neighbouring molecules. Thus O23 is involved in three of the four shortest distances between the molecules: O23–H10($1-x$, $x-\frac{1}{2}$, $\frac{1}{2}-z$): 2.47 Å, O23–H62 ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$): 2.68 Å and O23–H141 ($\frac{1}{2}+x$, $1\frac{1}{2}-y$, $1-z$): 2.60 Å. Finally, the distance N4–H22 is 2.44 Å.

It is seen from the tables 3,4 and 5 that there is very little difference in the geometry of the strychnine molecules in the two structures, except for the differences in the N4–C bonds which obviously are influenced by the protonation of the N4 atom. It appears that

protonation induces a lengthening of the N4–C bonds of about 0.04 Å. The small differences in angles may mostly be explained by these differences in bond lengths. The conformational characteristics of the strychnine molecule are described in Table 6.

It is interesting to note the magnitude of the N4–C3 bond (1.491 Å in strychnine and 1.539 in strychnine nitrate) which is rather long as compared to a similar bond in strychnofoline where the N4–C3 bond is found to be 1.450(7) Å.[12] However, in strychnofoline, which is a less rigid molecule than strychnine, the conformation about the N4–C3 bond is staggered, whereas the conformation about the N4–C3 bond in strychnine is eclipsed as shown by the stereograph in Fig. 5. Thus the results in the present study may indicate that eclipsing the groups bonded to N4 and C3, respectively, induces a lengthening of the N4–C3 bond of about $(2-4) \cdot 10^{-2}$ Å and that a quaternisation of the N4 atom in the eclipsed conformation may further increase the bond length by a similar magnitude. However, as clearly shown in Table 5 the overall conformational characteristics of the strychnine molecule is influenced very little indeed by the protonation of the N4 atom and the difference in molecular environment.

REFERENCES

1. Mostad, A. *Acta Chem. Scand. B 38* (1984) 381.
2. Mostad, A. *Acta Chem. Scand. B 38* (1984). 821.
3. Mostad, A., Mostad, H. and Rømming, C. *Acta Chem. Scand. B 39* (1985) 141.
4. Robertson, H.J. and Beevers, C.A. *Acta Crystallogr. 4* (1951) 270.
5. Bokhoven, C., Schoone, J.C. and Bijvoet, J.M. Acta *Crystallogr. 4* (1951) 275.
6. Doddahalli, S., Sake Gowda, Cartz, L. and Natarajan, S. *Acta Crystallogr. B 29* (1973) 2760.
7. Doyle, P.A. and Turner, R.S. *Acta Crystallogr. A 24* (1968) 390.
8. Stewart, R.F., Davidson, E.R. and Simpson, W.T. *J. Chem. Phys. 42* (1965) 3175.
9. Groth, P. *Acta Chem. Scand. 27* (1973) 1837.
10. Germain, G., Main, P. and Woolfson, M.M. *Acta Crystallogr. A 27* (1971) 368.
11. Gilmore, C.J. *J. Appl. Cryst. 17* (1984) 42.
12. Dideberg, O., Lamotte-Brasseur, J., Dupont, L., Campsteyn, H. and Vermeire, M. *Acta Crystallogr. 333* (1977) 1796.

Received January 14, 1985.