eluent (4:6 *v*/*v*)] to obtain 180 mg (71% yield) of compound (2) (R_f 0.47, M_r 236.43), which is a 97/3 mixture of the '*syn*' and '*anti*' stereoisomers. Compound (2) is relatively unstable in acid medium. Compound (2) was then used to prepare compound (3). Compound (2) (176 mg, 0.75 mmol; M_r 236), as the 97/3 mixture of '*syn*' and '*anti*' stereoisomers, and 4-dimethylaminopyridine (8 mg, 0.067 mmol; M_r 122) were dissolved in 2 ml of pyridine in a round-bottomed flask. 3,5-Dinitrobenzoyl chloride (DMAP) (170 mg, 0.74 mmol; M_r 230) was added under agitation in one shot and the reaction mixture left under agitation for 15 min, after which time it was extracted with diethyl ether and the organic phases washed three times with water, dried over Mg_2SO_4 and the solvent evaporated under reduced pressure to give the crude product (350 mg). This mixture, purified on chromatographic plates [silica gel, diethyl ether/pentane eluent (2:8 *v*/*v*)], led to a solid product (250 mg; R_f 0.46; m.p. 378–380 K). This product, recrystallized from a hot diethyl ether/pentane mixture, led to 200 mg (59.7% yield) of pure '*syn*' compound (3) ($C_{21}H_{26}N_2O_7Si$; M_r 446.54; m.p. 393–394 K; analysis found: C 56.32, H 5.81, N 6.24%; calculated: C 56.49, H 5.87, N 6.27%).

Crystal data

$C_{21}H_{26}N_2O_7Si$
$M_r = 446.53$
Monoclinic
$C2/c$
$a = 32.421\,(3)$ Å
$b = 6.235\,(1)$ Å
$c = 22.646\,(1)$ Å
$\beta = 91.333\,(7)°$
$V = 4576.5\,(9)$ Å^3
$Z = 8$
$D_x = 1.296$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40–50°$
$\mu = 1.285$ mm^{-1}
$T = 292\,(2)$ K
Parallelepiped
0.30 × 0.20 × 0.10 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.774$, $T_{max} = 0.879$
5404 measured reflections
4450 independent reflections

3734 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 71.81°$
$h = -39 \rightarrow 39$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 27$
3 standard reflections frequency: 60 min intensity decay: 4.0%

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.122$
$S = 1.110$
4450 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 1.6345P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.249$ e Å^{-3}
$\Delta\rho_{min} = -0.246$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.00080 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Si—O1	3.443 (1)		
O1—C1—C2—C3	83.9 (2)	C3—Si—O1—C1	9.78 (9)
C1—C2—C3—Si	−72.8 (2)	Si—O1—C1—C2	−38.8 (1)
C2—C3—Si—O1	24.6 (1)		

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*97.

The authors thank IBM Belgium, the Facultés Universitaires Notre-Dame de la Paix, and the FNRS, for the use of the Scientific Computing Facility. The authors thank Johan Wouters for help in collecting the data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1185). Services for accessing these data are described at the back of the journal.

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1,4-Dihydro-1-methyl-4-nitriminopyridine Dihydrate

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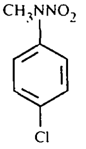
Abstract

Molecules of the title compound, $C_6H_7N_3O_2.2H_2O$, are almost planar with the NNO_2 nitrimino group twisted 8 (1)° out of the plane of the pyridine ring.

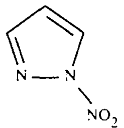
The nitrimino group and C_5N ring form a conjugated π-electron system. These molecules together with water molecules are arranged in planes. They are connected with each other by O—H···O, O—H···N and weaker C—H···O hydrogen bonds. Four water molecules form a planar square $(O—H···O—H)_2$ ring with O···O distances equal to 2.741 (2) and 2.778 (2) Å. These rings join pairs of molecular planes into double layers, interacting otherwise by van der Waals forces.

Comment

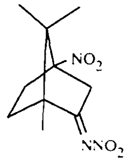
The organic derivatives of nitramide (NH_2NO_2) can be divided into four main groups: nitramines, *N*-nitroazoles, nitrimines and ylides. The molecular structures of these closely related compounds are different as illustrated below [(1)–(4)]. In 4-chloro-*N*-methylnitroaniline, (1), the Ar—N bond [1.423 (4) Å] is long, the length of the N—N bond [1.346 (3) Å] indicates a high bond order, and the nitramino group is nearly perpendicular to the aromatic ring (Ejsmont *et al.*, 1998). 1-Nitropyrazole, (2), is planar: the *N*-nitro group is twisted only 2 (1)° relative to the ring, along the N—N bond. The C—N [1.364 (3) Å] and N—N [1.399 (3) Å] bond lengths suggest that the *N*-nitro group and the heteroaromatic ring form one conjugated π-electron system (Tarımcı & Schempp, 1977). By contrast, in *N*,4-dinitrocamphorimine, (3), the C—N bond is of double character [1.273 (7) Å] and the *N*-nitro group is perpendicular to the C_3N plane (Cameron *et al.*, 1979); N—N is 1.461 (9) Å. The geometry of the *N*-nitro group in the pyridine 1-nitroimide molecule, (4), is nearly the same as in (1) (Arriau *et al.*, 1974); the coincidence of the bond lengths and angles is surprising [C—N 1.421 (3), N—N 1.341 (3) Å].



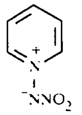
(1)



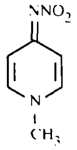
(2)



(3)



(4)



(5)

1,4-Dihydro-1-methyl-4-nitriminopyridine [(5), Fig. 1] belongs to the same nitrimine series as (3), but the molecular structures of (3) and (5) differ markedly. The length of the C—N bond [1.368 (2) Å] in (5) is similar to that in 1-nitropyrazole, (2), but the N—N bond [1.329 (2) Å] is significantly shorter. The NNO_2 group in (5) is twisted only 8 (1)° out of the plane of the pyridine ring. This small twist angle together with the short C—N and N—N bonds, indicate that the NNO_2 group forms a conjugated π-electron system with the C_5N ring. Hence the electronic structure of (5) may be considered as a resonance hybrid of three canonical forms. In two of them the pyridine ring has intact aromatic character.

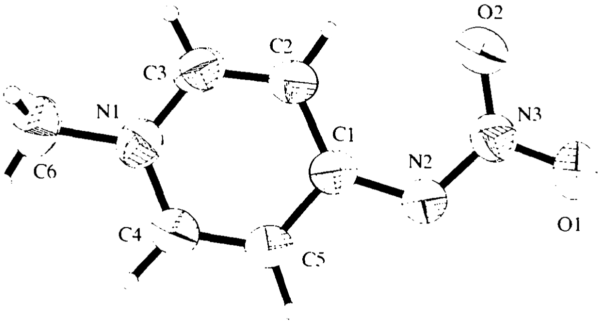


Fig. 1. The molecular structure of (5) with 50% probability ellipsoids for non-H atoms.

In the Cambridge Structural Database (Allen & Kennard, 1993) more than 17 000 compounds contain pyridine C_5N rings. The mean C—N bond length in the ring is 1.346 (3) Å, while the mean for the C—C ring bonds is 1.383 (8) Å. The C—N bond lengths in (5) [1.343 (3) Å] are essentially identical and equal to the mean C—N bond lengths in pyridine rings. The mean C2—C3 and C4—C5 bond lengths [1.350 (3) Å] are 0.03 Å shorter than the corresponding bond lengths in pyridine compounds, whereas the mean C1—C2 and C5—C1 bond lengths [1.402 (3) Å] are slightly larger (0.02 Å). The deviation of C—C bond lengths from the mean for the C—C lengths for pyridine reflects their higher or lower bond-order character. The differences are smaller than in 4-pyridone derivatives (Allen & Kennard, 1993) and indicate that the aromaticity of the pyridine ring is only slightly disturbed. The planar environment of the ring N1 atom is consistent with this model. Conjugation of the nitrimino group and pyridine ring may be responsible for the thermal stability of (5). It remains unchanged when heated to 523 K in DSC (differential scanning calorimetry), while its isomer *N*-methyl-*N*-(4-pyridyl)-1-nitramine rearranges exothermically at 443 K.

The molecular packing of 1,4-dihydro-1-methyl-4-nitriminopyridine dihydrate is shown in Fig. 2. The molecules of (5) and water are connected by O—H···N, O—H···O and C—H···O hydrogen bonds. The O—H···N and O—H···O bonds are of medium strength, whereas the C—H···O bonds are much weaker. Four water molecules joined by O—H···O hydrogen bonds form planar rings with O···O distances of 2.741 (2) and 2.778 (2) Å. These water rings join molecules of (5) into double layers, which are then connected by van der

Waals forces. The rings of water molecules lie almost perpendicular to the plane of the molecule of (5).

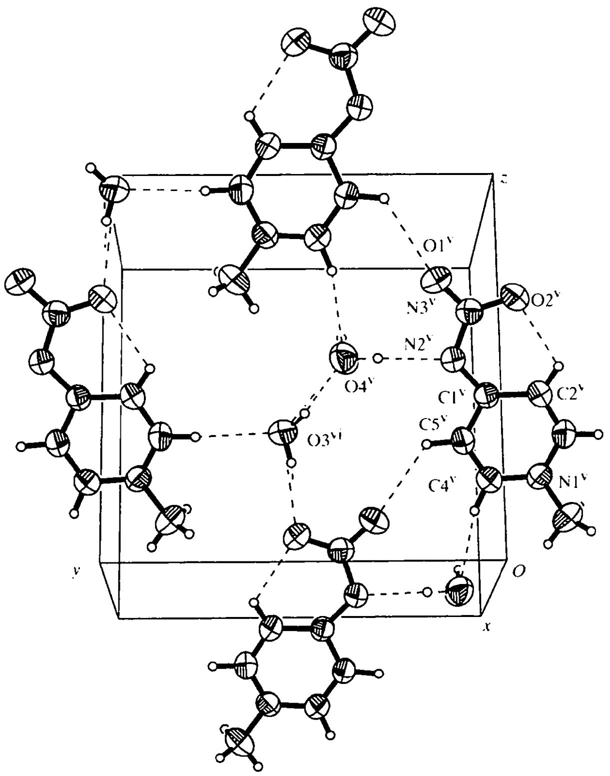


Fig. 2. The packing which shows layers of molecules of (5) and water with hydrogen bonding. Symmetry codes: (v) $x, y-1, z$; (vi) $-\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$.

Experimental

The title compound was obtained from *N*-(4-pyridyl)nitramine by methylation with dimethyl sulfate in an aqueous alkaline solution. The nitramine (2.78 g, 0.02 mol) was dissolved in 0.5 *M* aqueous potassium hydroxide (50 ml). Dimethyl sulfate (1.9 ml, 0.02 mol) and potassium carbonate (2.0 g, 0.02 mol) were added, the mixture was shaken until homogeneous and heated for 1 h with an additional portion (1.0 ml) of dimethyl sulfate. The solution was cooled to 253 K, a precipitate was collected by filtration and crystallized from methanol. Colourless transparent prisms (1.89 g, 62%) of (5) were obtained (m.p. 459–471 K). Crystals suitable for X-ray diffraction studies were grown by slow evaporation of water from an aqueous solution. Crystals of (5) begin to lose water of crystallization within a few minutes of being withdrawn from solution, crumbling into a white powder. The white powder has a melting point of 470 K (from DSC measurements), exactly the same as for crystals obtained from methanol solution. A suitable crystal was placed in a capillary containing a drop of mother liquor to prevent decomposition.

Crystal data

$C_6H_7N_3O_2.2H_2O$
$M_r = 189.18$
Monoclinic
$P2_1/n$
$a = 7.733(2)$ Å
$b = 10.648(2)$ Å
$c = 10.894(2)$ Å
$\beta = 90.09(3)°$
$V = 897.0(3)$ Å^3
$Z = 4$
$D_x = 1.401$ Mg m^{-3}
$D_m = 1.40(1)$ Mg m^{-3}
D_m measured by flotation method ($CHCl_3/CH_2Cl_2$)

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 7–12°$
$\mu = 0.118$ mm^{-1}
$T = 293(2)$ K
Irregular
$0.75 \times 0.60 \times 0.50$ mm
Colourless

Data collection

KM-4 Kuma diffractometer
ω–2θ scans
Absorption correction: none
3173 measured reflections
1554 independent reflections
1222 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$

$\theta_{\rm max} = 25.02°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 0$
2 standard reflections every 50 reflections intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.115$
$S = 1.096$
1554 reflections
163 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.0967P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.008$
$\Delta\rho_{\rm max} = 0.180$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.152$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.013 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—N2	1.368 (2)	C4—C5	1.351 (2)
C1—C5	1.400 (2)	C6—N1	1.470 (2)
C1—C2	1.403 (2)	N2—N3	1.329 (2)
C2—C3	1.349 (2)	N3—O2	1.239 (2)
C3—N1	1.343 (2)	N3—O1	1.240 (2)
C4—N1	1.343 (2)		
N2—C1—C5	113.78 (1)	C3—N1—C4	118.94 (1)
N2—C1—C2	130.95 (1)	C3—N1—C6	120.07 (2)
C5—C1—C2	115.27 (1)	C4—N1—C6	120.99 (2)
C3—C2—C1	120.34 (2)	N3—N2—C1	120.06 (1)
N1—C3—C2	122.57 (2)	O2—N3—O1	120.01 (1)
N1—C4—C5	120.75 (2)	O2—N3—N2	124.00 (1)
C4—C5—C1	122.09 (2)	O1—N3—N2	115.98 (1)
C5—C1—N2—N3	−173.0 (1)	C1—N2—N3—O2	0.1 (2)
C2—C1—N2—N3	7.8 (2)	C1—N2—N3—O1	179.0 (1)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.90 (2)	2.18 (2)	2.704 (2)	116 (2)
C3—H3···O3^{i}	0.91 (2)	2.38 (2)	3.280 (2)	170 (2)
C4—H4···O4^{ii}	0.95 (2)	2.52 (2)	3.441 (2)	163 (2)
C5—H5···O1^{ii}	0.96 (2)	2.57 (2)	3.242 (2)	127 (2)
O3—H31···O4^{iii}	0.87 (2)	1.89 (2)	2.741 (2)	166 (3)
O3—H32···O2	0.84 (2)	2.04 (2)	2.867 (2)	168 (2)
O4—H41···N2	0.89 (4)	1.97 (4)	2.859 (2)	176 (3)
O4—H42···O3^{iv}	0.84 (3)	1.95 (3)	2.778 (2)	168 (2)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}+x, \frac{5}{2}-y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, \frac{5}{2}-y, \frac{1}{2}+z$; (iv) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Data collection: *Kuma Diffraction Software* (Kuma, 1997). Cell refinement: *Kuma Diffraction Software.* Data reduction: *Kuma Diffraction Software.* Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL.* Software used to prepare material for publication: *SHELXL97.*

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1261). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1948-1951

Brucinium Hydrogen Fumarate Sesquihydrate and Brucinium Hydrogen Maleate

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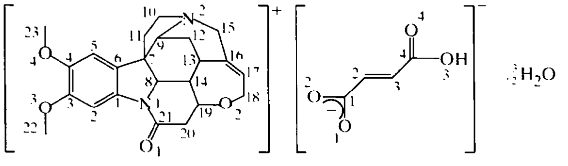
Abstract

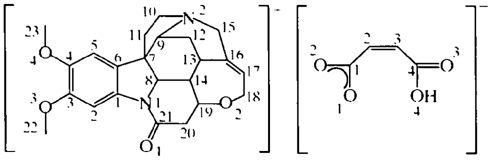
As part of a general study of brucine (alternative name: 2,3-dimethoxystrychnidine-10-one) as a co-crystallizing agent, the structures of its salts with the stereoisomeric fumaric and maleic acids are reported. The packing in the hydrogen fumarate, $C_{23}H_{27}N_2O_4\cdot C_4H_3O_4\cdot\frac{3}{2}H_2O$, is a variation of the corrugated sheet motif common to several brucine crystals, while the hydrogen maleate, $C_{23}H_{27}N_2O_4\cdot C_4H_3O_4$, shows a substantially different motif.

Comment

When structures contain substantial fragments of fixed and known stereochemistry, this may be used as a powerful aid in structure determination (Beurskens *et al.*, 1996). The natural alkaloid, brucine, possesses a well determined stereochemistry, and is therefore potentially very useful as a co-crystallizing agent for large molecules with acidic functions. The hydrogen fumarate, (I), and hydrogen maleate, (II), were obtained as background materials for such a programme. Structures containing brucine have a favoured, but far from universal, mode of packing (Dijksma *et al.*, 1998; Glover *et al.*, 1985; Gould *et al.*, 1984; Pinkerton *et al.*, 1993), in which ribbons of head-to-tail brucinium ions are packed parallel to one another to produce puckered sheets.



(I)



(II)

Both structures consist of equal numbers of brucinium ions and hydrogen fumarate or maleate ions. In (I), the brucinium cations are arranged in ribbons parallel to [010], as in the standard motif. Parallel ribbons (shaded light and dark) related by a twofold rotation axis are shown in Fig. 1. The resulting sheets are normal to [001]; the polarity of the ribbons is the same, but the direction of puckering is opposed. The general effect is to replace the characteristic corrugations with dimples.

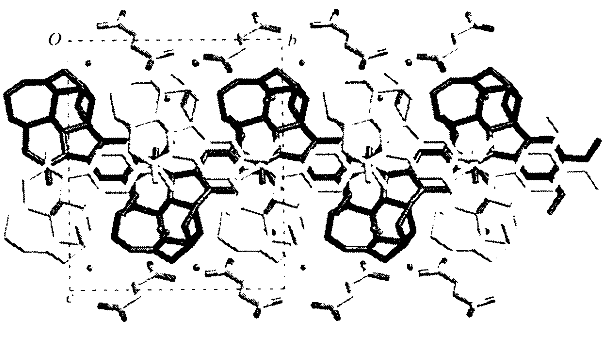


Fig. 1. Packing diagram of (I) viewed down the *a* axis. Short dashed lines indicate hydrogen-bonding interactions. H atoms are omitted for clarity.

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