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Structures of Strychnine (I), $C_{21}H_{22}N_2O_2$, and a Solvate of Brucine (II), $C_{23}H_{26}N_2O_4.C_2H_6O.2H_2O$

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Abstract. (I): $M_r = 334 \cdot 41$, $P2_12_12_1$, $a = 11 \cdot 267$ (2), $b = 11 \cdot 892$ (11), $c = 12 \cdot 105$ (4) Å, $V = 1622$ Å^3, $Z = 4$, $D_x = 1 \cdot 369$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 83$ cm^{-1}, $F(000) = 712$, $T = 290$ K, $R = 0 \cdot 037$, 1195 unique data. (II): $M_r = 476 \cdot 53$, $P2_12_12_1$, $a = 7 \cdot 723$ (1), $b = 12 \cdot 337$ (1), $c = 25 \cdot 212$ (2) Å, $V = 2403$ Å^3, $Z = 4$, $D_x = 1 \cdot 317$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 90$ cm^{-1}, $F(000) = 1024$, $T = 290$ K, $R = 0 \cdot 039$, 1684 unique data. Strychnine and brucine are related indole alkaloids. The molecular connectivities differ only in the OMe groups present in brucine. The molecular structures show significant conformational variations in the indole rings and in the six-membered ring containing the amide group, which is affected by hydrogen bonding in brucine, the latter crystallizing as a solvate.

Introduction. Strychnine and brucine are indole alkaloids isolated from the seeds of *Strychnos nux vomica* and related plants. The molecular connectivities are shown in Fig. 1 and differ only in the methoxy substituents [O(3), C(22), O(4) and C(23)] found only in brucine. A major use of strychnine and brucine has been the resolution of racemic mixtures of amino acids. The small chemical difference of the presence or absence of methoxy groups has a profound effect on the preferred crystal formed. For example, from a mixture of *N*-benzoyl-D,L-alanine, brucine preferentially crystallizes with the D-enantiomer, while strychnine crystallizes with the L-enantiomer. The methoxy groups also produce a marked reduction of physiological activity where the principal mode of action by both strychnine and brucine is by overstimulation of the central nervous system.

Although the structure of the cation of strychnine was reported in 1951 (Robertson & Beevers, 1951; Bokhoven, Schoone & Bijvoet, 1951) the free bases were considered too difficult for the methods then available. Crystals of strychnine are included in the compilation of Groth (1919) where the reported axial ratios 0·9827 and 0·9309 are clearly those of our crystals [0·9824 (4) and 0·9308 (10)]. The form of brucine reported by Groth is a tetrahydrate, different in structure from the form reported here.

Experimental. The strychnine crystals were obtained as well formed prisms from an aqueous solution of an equimolar mixture of strychnine and *N*-acetyl-L-phenylalanine. Similar deposition of strychnine crystals occurred from several mixtures of strychnine with *N*-acyl amino acids. Brucine crystals were obtained as colourless needles by recrystallizing commercial
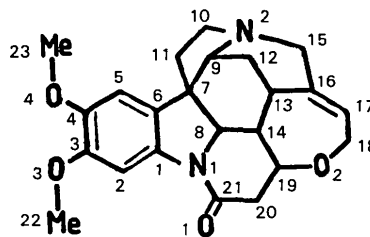

Fig. 1. Numbering scheme for atoms in (I) and (II).

Table 1. *Experimental data*

	(I)	(II)
Crystal dimensions (mm)	0·2 × 0·2 × 0·6	0·3 × 0·3 × 0·3
Reflections to determine lattice parameters	25	25
Max. $\sin\theta/\lambda$ (Å^{-1})	0·594	0·594
hkl range h:	0–13	0–9
k:	0–14	0–14
l:	0–14	0–29
Standard reflections	1,1,14	061; 0,0,12
drift correction range	0·99–1·02	0·98–1·04
Total data measured	1648	2459
Data used in refinement, $I > 2\sigma(I)$	1195	1684
Parameters refined	314	401
R	0·037	0·039
wR	0·053	0·054
S	1·6	0·9
Weighting-scheme parameter, A^*	0·0065	0·0017
Max. Δ/σ, last cycle	0·005	0·18
Final difference map (e Å^{-3}), max:	0·17	0·14
min:	−0·21	−0·14

brucine tetrahydrate from absolute ethanol. The crystals effloresce readily, and the crystal used for data collection was sealed in a Lindemann-glass tube with some added ethanol. Both data sets were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated radiation. Normal Lorentz–polarization corrections were applied, but no absorption or extinction correction. Other experimental data are summarized in Table 1. The structures were solved using the *MULTAN*77 system (Main, Lessinger, Woolfson, Germain & Declercq, 1977).

In both cases an easily recognizable fragment [all but one non-hydrogen atom in (I) and all but seven in (II)] was obtained from the map derived from the phase set with the highest figure of merit. The structures were completed and refined on F by standard methods. All non-hydrogen atoms were refined anisotropically and all H atoms of (I) were refined isotropically. Positional parameters were refined for all H atoms of (II) except for those bonded to the ethyl group of the ethanol solvent; these were restrained to calculated positions (C—H = 1·08 Å, fully staggered conformation). The brucine H atoms were refined with a common temperature factor, as were the H atoms of the solvent molecules. These temperature factors refined to 0·047 (8) and 0·175 (12) Å^2 respectively. Refinement of both structures was carried out using the *SHELX*76 program (Sheldrick, 1976). Molecular geometry was studied using *CALC* (Gould & Taylor, 1983) and diagrams were prepared using *PLUTO* (Motherwell, 1972) and an interactive version of *ORTEP* (Johnson, 1965; Mallinson, 1982). Positional and thermal parameters for (I) and (II) are listed in Tables 2 and 3.*

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* Anisotropic temperature factors, H-atom parameters, bond and angle data involving H atoms and lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39922 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Lists of bond lengths, angles, and torsion angles are given in Tables 4, 5 and 6. These, together with the molecular plots given as Fig. 2, show the close similarity of the two molecular geometries. The best fit of a strychnine molecule from (I) to the corresponding atoms of (II) gives an r.m.s. deviation of 0·051 Å. The major contributors to this difference are the atoms C(20) and O(1) of the amide ring [essentially a twist

Table 2. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *for* (I)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	−0·2946 (3)	0·3397 (3)	0·2632 (3)	0·0374
C(2)	−0·4172 (4)	0·3407 (5)	0·2471 (3)	0·0526
C(3)	−0·4661 (5)	0·2507 (6)	0·1887 (4)	0·0671
C(4)	−0·3982 (5)	0·1640 (5)	0·1481 (4)	0·0630
C(5)	−0·2768 (4)	0·1663 (4)	0·1629 (4)	0·0507
C(6)	−0·2247 (4)	0·2542 (3)	0·2204 (3)	0·0360
C(7)	−0·0957 (3)	0·2788 (3)	0·2384 (3)	0·0322
C(8)	−0·0992 (3)	0·3752 (3)	0·3253 (3)	0·0302
C(9)	−0·0165 (4)	0·1785 (3)	0·2713 (3)	0·0368
C(10)	0·0958 (4)	0·3102 (4)	0·1635 (4)	0·0445
C(11)	−0·0338 (4)	0·3172 (4)	0·1310 (3)	0·0382
C(12)	−0·0176 (4)	0·1515 (4)	0·3937 (4)	0·0416
C(13)	0·0226 (4)	0·2549 (3)	0·4576 (4)	0·0383
C(14)	−0·0761 (4)	0·3424 (3)	0·4456 (3)	0·0339
C(15)	0·1912 (4)	0·2205 (4)	0·3229 (4)	0·0525
C(16)	0·1434 (4)	0·2923 (4)	0·4152 (3)	0·0430
C(17)	0·1980 (4)	0·3825 (4)	0·4538 (4)	0·0510
C(18)	0·1437 (4)	0·4579 (4)	0·5390 (4)	0·0548
C(19)	−0·0679 (4)	0·4525 (3)	0·5127 (3)	0·0393
C(20)	−0·1668 (4)	0·5328 (4)	0·4776 (4)	0·0469
C(21)	−0·2619 (4)	0·4867 (4)	0·4038 (3)	0·0434
N(1)	−0·2234 (3)	0·41769 (25)	0·3205 (3)	0·0356
N(2)	0·1052 (3)	0·2091 (3)	0·2329 (3)	0·0451
O(1)	−0·3666 (3)	0·5103 (3)	0·4153 (3)	0·0679
O(2)	0·03974 (25)	0·51361 (24)	0·49800 (23)	0·0453

Table 3. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *for* (II)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0·6760 (5)	0·6173 (3)	0·25063 (13)	0·0343
C(2)	0·6937 (5)	0·5719 (3)	0·30152 (13)	0·0352
C(3)	0·7208 (5)	0·4621 (3)	0·30537 (13)	0·0377
C(4)	0·7331 (5)	0·3971 (3)	0·25869 (14)	0·0372
C(5)	0·7095 (5)	0·4431 (3)	0·20974 (14)	0·0369
C(6)	0·6793 (5)	0·5543 (3)	0·20585 (13)	0·0348
C(7)	0·6355 (5)	0·6214 (3)	0·15752 (13)	0·0327
C(8)	0·6612 (5)	0·7393 (3)	0·17854 (13)	0·0328
C(9)	0·7405 (5)	0·5956 (3)	0·10668 (14)	0·0401
C(10)	0·4537 (6)	0·6546 (4)	0·08297 (16)	0·0468
C(11)	0·4491 (5)	0·6046 (4)	0·13768 (16)	0·0406
C(12)	0·9158 (5)	0·6492 (3)	0·10441 (17)	0·0450
C(13)	0·8910 (5)	0·7730 (3)	0·10825 (15)	0·0420
C(14)	0·8313 (5)	0·7953 (3)	0·16513 (14)	0·0358
C(15)	0·7007 (7)	0·7198 (3)	0·03012 (15)	0·0490
C(16)	0·7663 (6)	0·8100 (3)	0·06503 (14)	0·0442
C(17)	0·7138 (6)	0·9115 (3)	0·06096 (16)	0·0480
C(18)	0·7639 (7)	0·9988 (4)	0·09865 (17)	0·0509
C(19)	0·8165 (5)	0·9139 (3)	0·18326 (15)	0·0405
C(20)	0·7429 (6)	0·9186 (3)	0·23941 (17)	0·0450
C(21)	0·7030 (5)	0·8141 (3)	0·26828 (15)	0·0420
C(22)	0·7169 (7)	0·4709 (4)	0·39897 (15)	0·0486
C(23)	0·7920 (9)	0·2226 (4)	0·22218 (19)	0·0608
N(1)	0·6565 (4)	0·72819 (22)	0·23718 (10)	0·0351
N(2)	0·6267 (4)	0·62933 (24)	0·06174 (11)	0·0438
O(1)	0·7157 (5)	0·80732 (21)	0·31678 (10)	0·0589
O(2)	0·7029 (3)	0·97784 (19)	0·15108 (10)	0·0459
O(3)	0·7390 (4)	0·40782 (19)	0·35169 (9)	0·0447
O(4)	0·7684 (4)	0·28948 (19)	0·26747 (10)	0·0482
O(1W1)	0·1081 (6)	0·0689 (3)	0·99054 (13)	0·0791
O(1W2)	0·0065 (6)	0·2122 (4)	0·90763 (17)	0·0974
C(1A)	0·0511 (10)	0·3619 (5)	0·03260 (22)	0·0966
C(2A)	−0·0108 (10)	0·2881 (6)	−0·07253 (25)	0·1091
O(1A)	−0·0615 (7)	0·3667 (4)	−0·01353 (15)	0·1006

Table 4. Bond lengths (Å) for (I) and (II)

	(I)	(II)		(I)	(II)		(I)	(II)
C(1)–C(2)	1·395 (6)	1·407 (5)	C(8)–C(14)	1·531 (5)	1·523 (5)	C(16)–C(17)	1·322 (6)	1·319 (6)
C(1)–C(6)	1·386 (5)	1·371 (5)	C(8)–N(1)	1·489 (5)	1·485 (4)	C(17)–C(18)	1·497 (7)	1·488 (6)
C(1)–N(1)	1·408 (5)	1·416 (4)	C(9)–C(12)	1·516 (6)	1·508 (6)	C(18)–O(2)	1·435 (6)	1·427 (5)
C(2)–C(3)	1·396 (8)	1·374 (5)	C(9)–N(2)	1·493 (6)	1·493 (5)	C(19)–C(20)	1·528 (6)	1·527 (6)
C(3)–C(4)	1·375 (8)	1·427 (5)	C(10)–C(11)	1·515 (6)	1·512 (6)	C(19)–O(2)	1·425 (5)	1·432 (5)
C(3)–O(3)		1·353 (4)	C(10)–N(2)	1·471 (6)	1·474 (5)	C(20)–C(21)	1·498 (6)	1·512 (6)
C(4)–C(5)	1·380 (7)	1·371 (5)	C(12)–C(13)	1·522 (6)	1·542 (6)	C(21)–N(1)	1·371 (5)	1·366 (5)
C(4)–O(4)		1·373 (4)	C(13)–C(14)	1·529 (5)	1·531 (5)	C(21)–O(1)	1·221 (6)	1·230 (5)
C(5)–C(6)	1·386 (6)	1·395 (5)	C(13)–C(16)	1·520 (6)	1·525 (6)	C(22)–O(3)		1·434 (5)
C(6)–C(7)	1·498 (5)	1·511 (5)	C(14)–C(19)	1·543 (5)	1·536 (5)	C(23)–O(4)		1·421 (6)
C(7)–C(8)	1·556 (5)	1·560 (5)	C(15)–C(16)	1·506 (6)	1·507 (6)	C(14)–C(2A)		1·439 (10)
C(7)–C(9)	1·542 (5)	1·550 (5)	C(15)–N(2)	1·464 (6)	1·485 (5)	C(14)–O(1A)		1·454 (8)
C(7)–C(11)	1·545 (5)	1·539 (5)						

Table 5. Bond angles (°) for (I) and (II)

	(I)	(II)		(I)	(II)		(I)	(II)
C(2)–C(1)–C(6)	121·1 (4)	121·6 (3)	C(7)–C(8)–C(14)	116·8 (3)	117·2 (3)	C(16)–C(17)–C(18)	122·7 (4)	123·8 (4)
C(2)–C(1)–N(1)	128·8 (4)	127·8 (3)	C(7)–C(8)–N(1)	104·3 (3)	104·4 (3)	C(17)–C(18)–O(2)	111·8 (4)	112·0 (4)
C(6)–C(1)–N(1)	110·1 (3)	110·6 (3)	C(14)–C(8)–N(1)	106·5 (3)	106·5 (3)	C(14)–C(19)–C(20)	109·9 (3)	109·9 (3)
C(1)–C(2)–C(3)	117·1 (4)	118·1 (3)	C(7)–C(9)–C(12)	114·2 (3)	114·3 (3)	C(14)–C(19)–O(2)	114·7 (3)	113·7 (3)
C(2)–C(3)–C(4)	122·4 (5)	120·4 (3)	C(7)–C(9)–N(2)	105·3 (3)	105·2 (3)	C(20)–C(19)–O(2)	105·5 (3)	106·0 (3)
C(2)–C(3)–O(3)		124·3 (3)	C(12)–C(9)–N(2)	111·3 (3)	112·2 (3)	C(19)–C(20)–C(21)	117·3 (4)	119·4 (3)
C(4)–C(3)–O(3)		115·3 (3)	C(11)–C(10)–N(2)	105·2 (3)	105·5 (3)	C(20)–C(21)–N(1)	115·6 (4)	116·0 (3)
C(3)–C(4)–C(5)	119·4 (5)	120·1 (3)	C(7)–C(11)–C(10)	101·6 (3)	102·7 (3)	C(20)–C(21)–O(1)	122·6 (4)	121·4 (4)
C(3)–C(4)–O(4)		115·0 (3)	C(9)–C(12)–C(13)	108·9 (3)	108·6 (3)	N(1)–C(21)–O(1)	121·8 (4)	122·7 (3)
C(5)–C(4)–O(4)		124·9 (3)	C(12)–C(13)–C(14)	106·5 (3)	105·9 (3)	C(1)–N(1)–C(8)	109·3 (3)	108·9 (3)
C(4)–C(5)–C(6)	120·0 (4)	119·5 (3)	C(12)–C(13)–C(16)	109·4 (3)	109·3 (3)	C(1)–N(1)–C(21)	125·2 (3)	125·7 (3)
C(1)–C(6)–C(5)	120·0 (4)	120·2 (3)	C(14)–C(13)–C(16)	114·8 (3)	115·2 (3)	C(8)–N(1)–C(21)	118·1 (3)	119·6 (3)
C(1)–C(6)–C(7)	110·7 (3)	110·5 (3)	C(8)–C(14)–C(13)	112·8 (3)	112·7 (3)	C(9)–N(2)–C(10)	108·1 (3)	108·5 (3)
C(5)–C(6)–C(7)	129·1 (4)	129·2 (3)	C(8)–C(14)–C(19)	107·1 (3)	107·6 (3)	C(9)–N(2)–C(15)	113·5 (3)	112·9 (3)
C(6)–C(7)–C(8)	102·6 (3)	102·0 (3)	C(13)–C(14)–C(19)	119·0 (3)	118·2 (3)	C(10)–N(2)–C(15)	113·4 (3)	112·7 (3)
C(6)–C(7)–C(9)	116·6 (3)	115·9 (3)	C(16)–C(15)–N(2)	111·6 (4)	111·7 (3)	C(18)–O(2)–C(19)	114·6 (3)	115·0 (4)
C(6)–C(7)–C(11)	111·9 (3)	113·5 (3)	C(13)–C(16)–C(15)	113·9 (4)	114·1 (3)	C(3)–O(3)–C(22)		115·9 (3)
C(8)–C(7)–C(9)	114·2 (3)	113·9 (3)	C(13)–C(16)–C(17)	122·3 (4)	122·3 (4)	C(4)–O(4)–C(23)		117·2 (3)
C(8)–C(7)–C(11)	111·2 (3)	110·8 (3)	C(15)–C(16)–C(17)	123·8 (4)	123·5 (4)	C(2A)–C(1A)–O(1A)		112·7 (6)
C(9)–C(7)–C(11)	100·6 (3)	101·2 (3)						

Table 6. Torsion angles (°) for (I) and (II)

	(I)	(II)		(I)	(II)		(I)	(II)
C(6)–C(1)–C(2)–C(3)	1·5 (6)	2·3 (5)	C(9)–C(7)–C(8)–C(14)	−26·9 (4)	−26·5 (4)	C(12)–C(13)–C(14)–C(8)	−60·3 (4)	−60·7 (4)
N(1)–C(1)–C(2)–C(3)	−178·5 (4)	−176·4 (3)	C(9)–C(7)–C(8)–N(1)	−144·1 (3)	−144·0 (3)	C(12)–C(13)–C(14)–C(19)	173·1 (3)	172·7 (3)
C(2)–C(1)–C(6)–C(5)	−1·7 (6)	−3·3 (5)	C(11)–C(7)–C(8)–C(14)	−139·9 (3)	−139·7 (3)	C(16)–C(13)–C(14)–C(8)	61·0 (4)	60·2 (4)
C(2)–C(1)–C(6)–C(7)	174·0 (4)	173·0 (3)	C(11)–C(7)–C(8)–N(1)	102·9 (3)	102·8 (3)	C(16)–C(13)–C(14)–C(19)	−65·7 (5)	−66·4 (4)
N(1)–C(1)–C(6)–C(5)	178·3 (4)	175·6 (3)	C(6)–C(7)–C(9)–C(12)	−83·6 (4)	−82·2 (4)	C(12)–C(13)–C(16)–C(15)	0·4 (5)	−0·3 (5)
N(1)–C(1)–C(6)–C(7)	−6·0 (4)	−8·2 (4)	C(6)–C(7)–C(9)–N(2)	154·0 (3)	154·3 (3)	C(12)–C(13)–C(16)–C(17)	177·8 (4)	176·0 (4)
C(2)–C(1)–N(1)–C(8)	174·2 (4)	174·1 (3)	C(8)–C(7)–C(9)–C(12)	36·0 (4)	35·7 (4)	C(14)–C(13)–C(16)–C(15)	−119·2 (4)	−119·3 (4)
C(2)–C(1)–N(1)–C(21)	25·0 (6)	21·4 (6)	C(8)–C(7)–C(9)–N(2)	86·5 (4)	−87·9 (3)	C(14)–C(13)–C(16)–C(17)	58·2 (6)	57·0 (5)
C(6)–C(1)–N(1)–C(8)	−5·8 (4)	−4·7 (4)	C(11)–C(7)–C(9)–C(12)	155·2 (3)	154·6 (3)	C(8)–C(14)–C(19)–C(20)	43·8 (4)	46·9 (4)
C(6)–C(1)–N(1)–C(21)	−155·1 (4)	−157·4 (3)	C(11)–C(7)–C(9)–N(2)	32·7 (4)	31·0 (3)	C(8)–C(14)–C(19)–O(2)	−74·9 (4)	−71·7 (4)
C(1)–C(2)–C(3)–C(4)	0·0 (8)	1·0 (5)	C(6)–C(7)–C(11)–C(10)	−167·5 (3)	−165·6 (3)	C(13)–C(14)–C(19)–C(20)	173·1 (3)	175·9 (3)
C(1)–C(2)–C(3)–O(3)		−179·6 (3)	C(8)–C(7)–C(11)–C(10)	78·4 (4)	80·5 (4)	C(13)–C(14)–C(19)–O(2)	54·4 (5)	57·3 (4)
C(2)–C(3)–C(4)–C(5)	−1·5 (8)	−3·2 (5)	C(9)–C(7)–C(11)–C(10)	−43·0 (4)	−40·7 (4)	N(2)–C(15)–C(16)–C(13)	52·5 (5)	52·4 (5)
C(2)–C(3)–C(4)–O(4)		177·0 (3)	C(7)–C(8)–C(14)–C(13)	40·1 (4)	40·5 (4)	N(2)–C(15)–C(16)–C(17)	−124·8 (5)	−123·8 (4)
O(3)–C(3)–C(4)–C(5)		177·3 (3)	C(7)–C(8)–C(14)–C(19)	172·8 (3)	172·5 (3)	C(16)–C(15)–N(2)–C(9)	−48·2 (5)	−47·3 (4)
O(3)–C(3)–C(4)–O(4)		−2·5 (4)	N(1)–C(8)–C(14)–C(13)	156·0 (3)	156·9 (3)	C(16)–C(15)–N(2)–C(10)	75·7 (5)	76·1 (4)
C(2)–C(3)–O(3)–C(22)		4·0 (5)	N(1)–C(8)–C(14)–C(19)	−71·2 (3)	−71·1 (3)	C(13)–C(16)–C(17)–C(18)	−2·5 (7)	−2·4 (6)
C(4)–C(3)–O(3)–C(22)		−176·5 (3)	C(7)–C(8)–N(1)–C(1)	14·5 (4)	14·9 (3)	C(15)–C(16)–C(17)–C(18)	174·7 (4)	173·5 (4)
C(3)–C(4)–C(5)–C(6)	1·3 (8)	2·2 (5)	C(7)–C(8)–N(1)–C(21)	166·2 (3)	169·5 (3)	C(16)–C(17)–C(18)–O(2)	−65·2 (6)	−62·9 (6)
O(4)–C(4)–C(5)–C(6)		−178·1 (3)	C(14)–C(8)–N(1)–C(1)	−109·6 (3)	−109·8 (3)	C(17)–C(18)–O(2)–C(19)	88·2 (4)	87·6 (4)
C(3)–C(4)–O(4)–C(23)		−176·4 (3)	C(14)–C(8)–N(1)–C(21)	42·1 (4)	44·8 (4)	C(14)–C(19)–C(20)–C(21)	10·1 (5)	2·0 (5)
C(5)–C(4)–O(4)–C(23)		3·8 (5)	C(7)–C(9)–C(12)–C(13)	−58·3 (4)	−58·5 (4)	O(2)–C(19)–C(20)–C(21)	134·3 (4)	125·1 (4)
C(4)–C(5)–C(6)–C(1)	0·2 (7)	1·0 (5)	N(2)–C(9)–C(12)–C(13)	60·8 (4)	61·2 (4)	C(14)–C(19)–O(2)–C(18)	−66·0 (4)	−69·0 (4)
C(4)–C(5)–C(6)–C(7)	−174·5 (4)	−174·5 (3)	C(7)–C(9)–N(2)–C(10)	−9·9 (4)	−9·7 (4)	C(20)–C(19)–O(2)–C(18)	172·8 (3)	170·2 (3)
C(1)–C(6)–C(7)–C(8)	14·5 (4)	16·6 (4)	C(7)–C(9)–N(2)–C(15)	116·8 (4)	116·0 (3)	C(19)–C(20)–C(21)–N(1)	−41·7 (5)	−30·0 (5)
C(1)–C(6)–C(7)–C(9)	140·1 (3)	140·9 (3)	C(12)–C(9)–N(2)–C(10)	−134·2 (3)	−134·6 (3)	C(19)–C(20)–C(21)–O(1)	139·5 (4)	148·5 (4)
C(1)–C(6)–C(7)–C(11)	−104·9 (4)	−102·6 (4)	C(12)–C(9)–N(2)–C(15)	−7·5 (5)	−8·9 (4)	C(20)–C(21)–N(1)–C(1)	159·9 (4)	154·8 (3)
C(5)–C(6)–C(7)–C(8)	−170·4 (4)	−167·6 (4)	N(2)–C(10)–C(11)–C(7)	38·2 (4)	35·9 (4)	C(20)–C(21)–N(1)–C(8)	13·1 (5)	4·7 (5)
C(5)–C(6)–C(7)–C(9)	−44·8 (6)	−43·2 (5)	C(11)–C(10)–N(2)–C(9)	−17·8 (4)	−16·4 (4)	O(1)–C(21)–N(1)–C(1)	−21·3 (6)	−23·7 (4)
C(5)–C(6)–C(7)–C(11)	70·3 (5)	73·3 (5)	C(11)–C(10)–N(2)–C(15)	−144·6 (4)	−142·2 (3)	O(1)–C(21)–N(1)–C(8)	−168·1 (4)	−173·8 (3)
C(6)–C(7)–C(8)–C(14)	100·3 (3)	99·2 (3)	C(9)–C(12)–C(13)–C(14)	69·2 (4)	69·8 (4)			
C(6)–C(7)–C(8)–N(1)	−16·9 (3)	−18·3 (3)	C(9)–C(12)–C(13)–C(16)	−55·4 (4)	−54·9 (4)			

about the C(21)—N(1) bond] with deviations of 0·13 and 0·15 Å respectively. When these are removed, the r.m.s. deviation of the remaining atoms drops to 0·033 Å, with a maximum of 0·055 Å [C(11)]. The divergence in the amide ring is also shown by the variation of torsion angles (Table 6). These vary by about ±3° with the exception of those about the bonds C(19)—C(20) and C(20)—C(21) which vary by between 8 and 12°. Although changes in bond angles are small, there are differences of 1·5° in the angles C(20)—C(21)—N(1) and C(8)—N(1)—C(21), both of which tend to make the ring flatter in (II). [The r.m.s. deviation of the atoms for the plane defined by N(1), C(8), C(19), C(20) and C(21) is 0·17 Å in (I) and 0·14 Å in (II)]. At the same time the amide group defined by C(1), C(8), C(20), C(21), N(1) and O(1) becomes less planar [r.m.s. deviation 0·09 Å in (I), 0·11 Å in (II)]. These deviations are doubtless connected with the hydrogen bonding at O(1) in (II), which is discussed below. The seven-membered rings [defined by C(19), C(14), C(13), C(16), C(17), and O(2)] show no significant variation between the two structures, although it might be supposed that this is the most flexible part of the molecules. Similarly, there is no significant variation in bond lengths at N(2), the amine N, although it is involved in hydrogen bonding in (II) and not in (I).

There is, however, a significant difference in the indole ring system between the two compounds. The benzene ring is planar in both compounds [r.m.s. deviation 0·008 Å in (I), 0·014 Å in (II)] and the azole ring less so [r.m.s. deviation 0·076 Å in (I), 0·083 Å in (II)]. The interplanar angle is 4·6° in (I) and 6·6° in (II). The most marked difference is the alternation of long and short bonds about the benzene ring in (II). The average bond length is 1·386 (7) Å in (I) and 1·391 (21) Å in (II). The differences in bond lengths (II—I) may be seen in Table 4. The major difference occurs at the bond separating the two methoxy groups in (II), which has much greater single-bond character as

a result. The methoxy groups are almost coplanar with the benzene ring; they deviate to opposite sides with the deviations from the plane being: O(3) —0·045, C(22) —0·157, O(4) +0·068, C(23) +0·182 Å.

Molecular packing

There is no possibility for hydrogen bonding in (I), and the packing in the crystal is governed by molecular shape and van der Waals interactions. This contrasts with the arrangements found in the crystal structures of all strychinine salts with simple anions (Cleasby, Gould, Moulden, & Walkinshaw, 1981) where anions and water molecules form distinct hydrophilic sheets, separating bilayers of strychnine molecules. In that arrangement, the amine nitrogen [N(2)] is protonated, and contributes to specific hydrogen bonds. In the free base (Fig. 3), there is no obvious bilayer structure, and van der Waals contacts are evenly distributed around the molecules. Short intermolecular contacts are summarized in Table 7. The short C—C contacts (as well as the related short C—H contacts) all involve either aromatic or olefinic C atoms. The contact C(2)···C(20) is interesting in that one of the H atoms bonded to C(20) is almost directly above the centre of an aromatic ring, making contacts ranging from 2·8 to 3·5 Å with all the ring C atoms. This arrangement is also found in solid benzene (Beevers, 1976) where it was interpreted as a favourable electrostatic interaction between the proton and the π cloud of the aromatic ring.

The methylene carbon, C(20), is also involved in the shortest C···N contact, and the H atom not involved in the interaction with the aromatic ring is only 2·53 (6) Å from N(2). The shortest contact of all, not involving H, is C(4)···O(1), and the H atom bonded to C(4) is 2·41 (6) Å from O(1). In both of these cases there is an interaction between H and an electronegative atom, which in (II) is a conventional hydrogen-bond acceptor.

Crystal packing in (II) is indeed dominated by hydrogen bonding between solvent molecules and acceptor carbonyl [O(1)] or amine [N(2)] groups on brucine. All protons bonded to O are used in hydrogen
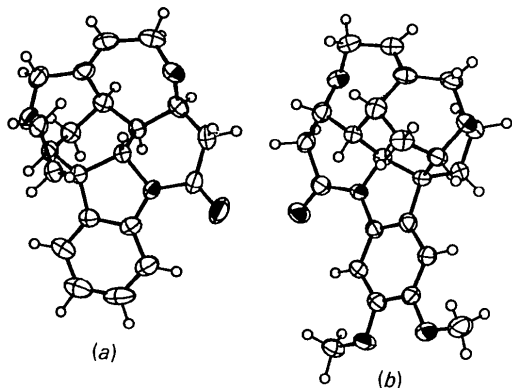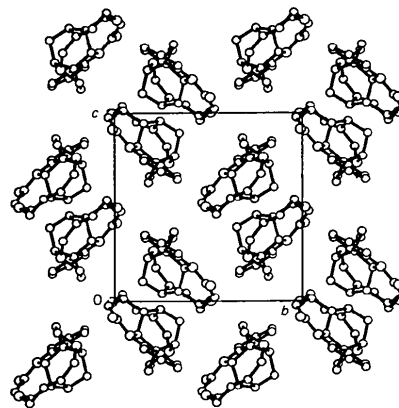

Fig. 2. Perspective drawings of (a) a strychnine molecule (I) and (b) a brucine molecule (II). Non-hydrogen atoms are shown as 50% probability thermal ellipsoids, and O and N atoms are shaded.

Fig. 3. Projection of (I) along **a**.

Table 7. *Intermolecular contacts not involving* H *atoms or solvent molecules up to* 3·72 Å; *distances are in* Å *and have approximate e.s.d.'s of* 0·008 Å

Type	(I)		Symmetry*	(II)		Symmetry*
C–C	3·715	C(4)–C(11)	1	3·556	C(17)–C(22)	7
	3·716	C(2)–C(20)	2	3·588	C(4)–C(21)	8
	3·720	C(12)–C(17)	3	3·606	C(5)–C(21)	8
				3·636	C(3)–C(19)	9
				3·689	C(4)–C(20)	8
C–N	3·372	C(20)–N(2)	4	3·614	C(23)–N(1)	8
	3·584	C(21)–N(2)	4	3·663	C(4)–N(1)	8
C–O	3·310	C(4)–O(1)	5	3·459	C(3)–O(2)	8
	3·456	C(12)–O(1)	6	3·459	C(13)–O(3)	10
	3·505	C(11)–O(1)	2	3·483	C(22)–O(2)	8
	3·648	C(3)–O(1)	5	3·488	C(2)–O(2)	8
				3·530	C(14)–O(4)	10
				3·547	C(19)–O(3)	10
				3·576	C(23)–O(2)	11
				3·624	C(14)–O(3)	10
				3·643	C(8)–O(4)	7
				3·708	C(11)–O(4)	7
N–N	—			—		
N–O	—			3·372	N(1)–O(4)	9
O–O	—			3·524	O(2)–O(3)	7

* Symmetry operations (applied to the second named atoms)

(1) x−½, ½−y, z̄   (2) x̄−½, 1−y, z−½
(3) x−½, ½−y, 1−z   (4) x̄, ½+y, ½−z
(5) x̄−1, y−½, ½−z   (6) ½+x, ½−y, 1−z
(7) 1−x, ½+y, ½−z   (8) 1−x, y−½, ½−z
(9) 2−x, y−½, ½−z   (10) 2−x, ½+y, ½−z
(11) x, y−1, z

N(2)   O(1)
:   :
1.89 (11) :   : 2.875 (6)
:   :
H   H
| 2.24 (11) H   2.800 (8)
O(1W1) — H ·········· O(1W2)— H ········· O(1A) — Et
: |
1.72 (11) :   : 2.736 (7)
:   H
H   :
| :
Et — O(1A) — H ········· O(1W2) — H ········ O(1W1)
1.89 (11) | 2.847 (7) |
1.85 (11) :   : 2.789 (6)
:   :
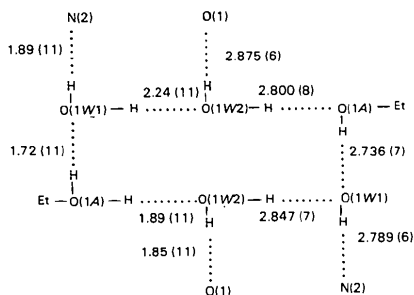O(1)   N(2)

Fig. 4. Schematic representation of the hydrogen bonding in (II). Figures on the right are O···N or O···O distances (Å); those on the left are O···H or N···H distances (Å). Each circuit implies an advance of a (7·723 Å).
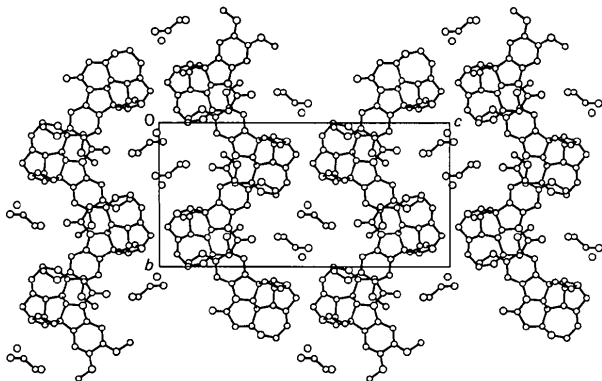

Fig. 5. Projection of (II) along **a**.

bonding, which is shown schematically in Fig. 4. The solvent molecules form helices up the 2$_1$ axes parallel to **a** at x, ¼, 0 and x, ¾, ½. The brucine molecules link these helices together, as each accepts a hydrogen bond at N(2) from one helix and at O(1) from the other. Neither the amide nitrogen [N(1)] nor the ether oxygens [O(2), O(3) and O(4)] are involved in hydrogen bonding.

The molecular packing, shown in Fig. 5, may be described as corrugated monolayers of brucine molecules separated by the hydrogen-bonded solvent network. This arrangement is also found in other structures containing brucine, and is reflected in cell dimensions, which have similar short and intermediate axes to (II), preserving the corrugated sheets, and show variability in the long axis, which adjusts to fit the 'guest' molecules. Examples are brucine + N-benzoyl-L-alanine (Gould & Walkinshaw, 1984) with c = 8·222, a = 12·423, b = 33·343 Å, and brucine + 1-(o-bromo-phenyl)-1-phenyl-2-propyn-1-ol (Toda, Tanaka & Ueda 1981) with c = 7·728, a = 12·446, b = 33·446 Å.

Short intermolecular contacts *not* involving hydrogen bonding are given in Table 7. None of these are interlayer contacts. All 19 contacts given involve the methoxy groups or atoms C(2) to C(5) of the aromatic ring. The two methoxy groups give the brucine molecule a longer wedge shape than is found in strychnine, and the corrugated sheets formed by brucine may well be governed by the the the drive to pack the wedges efficiently.

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