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Staphisine

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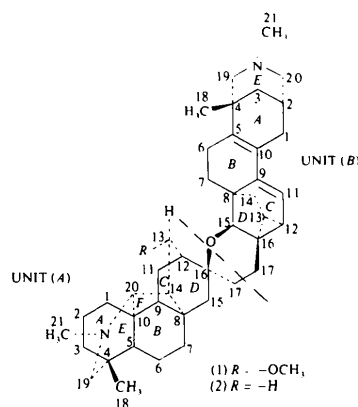
Abstract

The crystal structure of staphisine, $C_{43}H_{60}N_2O_2$, has been determined by direct methods and refined by block-diagonal least squares to $R = 0.049$ and $R_w = 0.068$ for 2529 observed reflections. The crystals are orthorhombic, space group $P2_12_12_1$, $a = 16.122$ (9), $b = 25.490$ (15), $c = 8.822$ (4) Å, $D_m = 1.150$ and $D_x = 1.165$ Mg m $^{-3}$ ($Z = 4$). The 3858 unique reflections with $2\theta \leq 140^\circ$ were measured using Cu $K\alpha$ radiation on an automated four-circle diffractometer. The compound is composed of two diterpene alkaloid-like units. One of the units may have undergone prior rearrangement which modified its ring system and produced a nonplanar diene functionality. Steric interaction of the methoxy group with an *N*-methyl appears to be responsible for the shift in 1H NMR resonance for the *N*-methyl relative to its resonance in the non-methoxy companion alkaloid, staphidine.

Introduction

Staphisine was first isolated in 1941 from the seeds of *Delphinium staphisagria* and at that time was tentatively assigned the molecular formula $C_{44}H_{60}N_2O$ (Jacobs & Craig, 1941). Its molecular formula was later corrected to $C_{43}H_{60}N_2O_2$ on the basis of an X-ray diffraction study of its monomethiodide (Pelletier, Kapadi, Wright, Page & Newton, 1972). The study showed staphisine to be a combination of two atisine-type diterpene alkaloid molecules. Puzzling at the time were the unusually low microanalyses for methoxy and the unclearness of the methoxy group in electron density maps. Subsequently it was discovered that the

staphisine sample had actually been a mixture of staphisine (1) and the non-methoxy alkaloid staphidine (2) (Pelletier, Mody, Djarmati, Mićović & Thakkar, 1976). The crystal used for the X-ray study, while primarily staphisine methiodide, had also contained some of the staphidine derivative. A method of cleanly separating the two alkaloids was devised and crystals of pure staphisine were obtained. A more accurate X-ray crystallographic study of staphisine was then accomplished using these crystals and the details of the analysis are presented here.



Experimental

A crystal of approximate dimensions $0.6 \times 0.3 \times 0.1$ mm was chosen for the X-ray experiment. Crystal data are listed in Table I. Cell constants were determined by a least-squares fit to precisely measured θ values of 15 reflections. The space group was unambiguously determined from the systematic absence of $h00, 0k0$,

Table 1. *Crystal data*

Staphisine, $C_{43}H_{60}N_2O_2$, $M_r = 637.02$, m.p. = 484–486 K, orthorhombic, $P2_12_12_1$, $a = 16.122$ (9), $b = 25.490$ (15), $c = 8.822$ (4) Å, $V = 3625.4$ Å³, $D_x = 1.165$ ($Z = 4$), $D_m = 1.150$ Mg m⁻³, $F(000) = 1392$, $\mu = 0.546$ mm⁻¹ (Cu $K\alpha$, $\lambda = 1.5418$ Å)

and $00l$ reflections, where h , k , and l are odd. Integrated intensities for the unique reflections with $2\theta \leq 140^\circ$ were measured on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Of the 3858 reflections measured, 2529 (65%) were considered observed after correcting for Lorentz and polarization effects [$I \geq 2\sigma(I)$]. Because of the small absorption coefficient calculated for the crystal, no absorption corrections were made.

Structure solution and refinement

The structure was solved by application of a multiple-solution tangent-formula procedure (Germain, Main & Woolfson, 1971). A hand-picked starting set, including three origin-determining reflections and three general reflections of unknown phase, was used to determine possible phases for the 680 reflections with $|E| > 1.3$, and one of the generated phase sets yielded the solution of the structure.

The structure was refined using a block-diagonal least-squares procedure where the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ and an empirical weighting scheme, $w = \{1.0 + [(|F_o| - 12.0)/6.0]^2\}^{-1}$, was employed (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). All non-hydrogen atoms were refined with anisotropic thermal parameters, while the hydrogens, which were located on difference maps, were isotropically refined. The scattering factors of Cromer & Mann (1968) were used for non-hydrogens and those of Stewart, Davidson & Simpson (1965) for hydrogens. During the final stages of refinement the effects of secondary extinction were minimized by including an isotropic extinction coefficient (Larson, 1967). At this point, seven reflections with low 2θ values which still showed wide discrepancies between their observed and calculated structure factors were removed from the data set.

Refinement was considered complete when the maximum shift/error for all variables, excluding the overall temperature factor and the extinction coefficient (which were highly correlated), was 1.54, and the average shift/error for all the variables was 0.33. A final difference map was featureless, showing no peaks greater than $0.17 e \text{ \AA}^{-3}$ and no holes greater than $0.19 e \text{ \AA}^{-3}$. The final unweighted and weighted residuals, $R = \sum |\Delta F| / \sum |F_o|$, $R_w = (\sum w|\Delta F|^2 / \sum |F_o|^2)^{1/2}$, were 0.049 and 0.068, respectively.

Discussion of the structure

Staphisine is a bis-diterpene alkaloid consisting of two atisine-type units, designated (*A*) and (*B*), joined to form a central six-membered ring. While it is tempting to think of the compound as a condensation product of two diterpenoid alkaloid molecules, there is currently no information on the biosynthesis of the bis-diterpene alkaloids to support this hypothesis. Rings *A* and *E* of unit (*A*) are fused in the fashion characteristic of diterpenoid alkaloids, but the *A*–*F* ring junction in unit (*B*) is atypical, C(20*B*) being bonded to C(2*B*) rather than to C(10*B*). This novel ring junction is a feature shared by several other bis-diterpene alkaloids isolated from *D. staphisagria*, but one not present in any of the known diterpenoid alkaloids (Pelletier & Mody, 1980). It is possible that unit (*B*) originally had one of the known atisine-type skeletons which rearranged to give the uncharacteristic ring fusion. Interestingly, two of the bis-diterpene alkaloids isolated from *D. staphisagria* have normal *A*–*E* ring junctions in both their units (Pelletier & Mody, 1980). One of these compounds is identical to staphisine except in this respect, the presence of an oxazolidine ring in unit (*B*) and the absence of a C(5*B*)–C(10*B*) double bond.

The three-membered ring in unit (*B*) is an unusual feature which may also be the result of a rearrangement. It has, in fact, a precedent in the rearrangement product of the atisine-type diterpene alkaloid, hetisine (Wright, Newton & Pelletier, 1969). Reduction of a hetisine derivative mesylated at C(13) (assuming the same numbering scheme used for staphisine) resulted in the formation of a C(13)–C(16) bond and, consequently, a three-membered ring in the *C*–*D* ring system of the molecule.

Staphisine's one methoxy group is *endo* with respect to ring *D* of unit (*A*). This is the same configuration which was assigned on the basis of ¹H NMR data. The ¹H NMR signal for the *N*-methyl group in unit (*A*) was shifted 0.06 p.p.m. upfield for staphidine with respect to the same signal for staphisine (Pelletier *et al.*, 1976). The difference was attributed to steric interaction of the hydrogens on the unit (*A*) *N*-methyl with the methoxy group. Inspection of molecular models showed the closest approach of the methoxy and *N*-methyl groups would occur when the methoxy group had the configuration indicated by our X-ray study. The actual C(21*A*)–C(22*A*) distance in the crystal structure is 4.103 (8) Å, but free rotation of the methoxy group would allow C(22*A*) a closer approach to the *N*-methyl. The distance of the methoxy oxygen from the *N*-methyl is 4.539 (7) Å.

The diene system is distinctly nonplanar [C(11*B*)–C(9*B*)–C(10*B*)–C(5*B*) = 155°] presumably because of the strained ring system. The deviation from planarity corresponds to an approximate 18° rotation of the planar group of atoms [C(8*B*), C(9*B*),

Table 2. Fractional coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for the non-hydrogen atoms of staphisine with *e.s.d.*'s in parentheses

A and *B* refer to the unit of the molecule to which the atom belongs.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1 <i>A</i>)	1819 (3)	3712 (2)	1691 (6)	64 (4)
C(2 <i>A</i>)	1374 (3)	4171 (2)	975 (7)	79 (5)
C(3 <i>A</i>)	1257 (4)	4081 (2)	-691 (8)	95 (7)
C(4 <i>A</i>)	2076 (3)	3954 (2)	-1493 (6)	78 (5)
C(5 <i>A</i>)	2471 (3)	3457 (1)	-781 (5)	66 (5)
C(6 <i>A</i>)	3244 (3)	3284 (2)	-1672 (5)	78 (5)
C(7 <i>A</i>)	3826 (3)	2947 (1)	-754 (5)	62 (4)
C(8 <i>A</i>)	3910 (2)	3083 (1)	938 (4)	47 (3)
C(9 <i>A</i>)	3057 (2)	3089 (1)	1692 (4)	43 (3)
C(10 <i>A</i>)	2641 (2)	3565 (1)	910 (5)	52 (4)
C(11 <i>A</i>)	3182 (2)	3176 (1)	3421 (4)	47 (3)
C(12 <i>A</i>)	4102 (2)	3200 (1)	3844 (4)	45 (3)
C(13 <i>A</i>)	4438 (3)	3678 (1)	2965 (5)	53 (4)
C(14 <i>A</i>)	4152 (2)	3658 (1)	1290 (5)	50 (3)
C(15 <i>A</i>)	4539 (2)	2698 (1)	1623 (5)	50 (3)
C(16 <i>A</i>)	4512 (2)	2677 (1)	3334 (5)	45 (3)
C(17 <i>A</i>)	5361 (2)	2557 (1)	4006 (5)	57 (4)
C(18 <i>A</i>)	1909 (5)	3862 (2)	-3196 (7)	122 (10)
C(19 <i>A</i>)	2682 (4)	4411 (2)	-1265 (6)	86 (5)
C(20 <i>A</i>)	3343 (3)	3982 (1)	1014 (5)	55 (3)
C(21 <i>A</i>)	3897 (4)	4787 (2)	-8 (8)	105 (8)
C(22 <i>A</i>)	5648 (3)	4213 (2)	2934 (7)	80 (5)
N(<i>A</i>)	3415 (3)	4311 (1)	-344 (5)	73 (5)
O(<i>A</i>)	5320 (2)	3709 (1)	3155 (4)	70 (4)
C(1 <i>B</i>)	3302 (2)	505 (1)	2553 (4)	43 (3)
C(2 <i>B</i>)	2688 (3)	320 (1)	1351 (4)	47 (3)
C(3 <i>B</i>)	2371 (3)	792 (1)	507 (5)	52 (4)
C(4 <i>B</i>)	1851 (2)	1125 (1)	1605 (4)	46 (3)
C(5 <i>B</i>)	2374 (2)	1276 (1)	2967 (4)	38 (3)
C(6 <i>B</i>)	2104 (2)	1750 (1)	3848 (5)	46 (4)
C(7 <i>B</i>)	2418 (2)	1743 (1)	5458 (5)	48 (3)
C(8 <i>B</i>)	3341 (2)	1646 (1)	5541 (4)	40 (3)
C(9 <i>B</i>)	3628 (2)	1206 (1)	4520 (4)	36 (3)
C(10 <i>B</i>)	3050 (2)	1005 (1)	3359 (4)	36 (3)
C(11 <i>B</i>)	4424 (2)	1082 (1)	4647 (5)	45 (3)
C(12 <i>B</i>)	4935 (2)	1403 (1)	5690 (5)	51 (4)
C(13 <i>B</i>)	4558 (3)	1608 (1)	7157 (5)	55 (3)
C(14 <i>B</i>)	3633 (2)	1522 (1)	7191 (4)	49 (3)
C(15 <i>B</i>)	3897 (2)	2125 (1)	5220 (4)	40 (3)
C(16 <i>B</i>)	4725 (2)	1981 (1)	5876 (5)	49 (3)
C(17 <i>B</i>)	5360 (2)	2404 (1)	5693 (5)	59 (4)
C(18 <i>B</i>)	1526 (3)	1608 (2)	733 (6)	69 (5)
C(19 <i>B</i>)	1118 (2)	791 (1)	2113 (5)	54 (3)
C(20 <i>B</i>)	1960 (3)	6 (1)	1977 (5)	54 (4)
C(21 <i>B</i>)	681 (3)	-9 (2)	3318 (6)	74 (5)
N(<i>B</i>)	1388 (2)	315 (1)	2897 (4)	51 (3)
O(<i>B</i>)	3948 (1)	2247 (1)	3656 (3)	39 (2)

C(11*B*),C(12*B*)] about bond C(8*B*)—C(9*B*). Not surprisingly, the two double bonds are somewhat shorter and the single bond C(9*B*)—C(10*B*) is longer than would be expected in an unhindered conjugated system [see, for example, Sly (1964) and Stam & MacGillivray (1963)].

Staphisine's ring system has only a few flexible areas, the most significant of which is the central oxygen-containing ring. The junction of this ring with unit (*B*)

Table 3. Bond distances (\AA) with *e.s.d.*'s in parentheses

C(1 <i>A</i>)—C(2 <i>A</i>)	1.511 (7)	C(22 <i>A</i>)—O(<i>A</i>)	1.404 (5)
C(1 <i>A</i>)—C(10 <i>A</i>)	1.541 (6)	C(1 <i>B</i>)—C(2 <i>B</i>)	1.526 (5)
C(2 <i>A</i>)—C(3 <i>A</i>)	1.500 (9)	C(1 <i>B</i>)—C(10 <i>B</i>)	1.514 (5)
C(3 <i>A</i>)—C(4 <i>A</i>)	1.533 (8)	C(2 <i>B</i>)—C(3 <i>B</i>)	1.505 (5)
C(4 <i>A</i>)—C(5 <i>A</i>)	1.549 (6)	C(2 <i>B</i>)—C(20 <i>B</i>)	1.523 (6)
C(4 <i>A</i>)—C(18 <i>A</i>)	1.544 (8)	C(3 <i>B</i>)—C(4 <i>B</i>)	1.538 (5)
C(4 <i>A</i>)—C(19 <i>A</i>)	1.535 (7)	C(4 <i>B</i>)—C(5 <i>B</i>)	1.517 (5)
C(5 <i>A</i>)—C(6 <i>A</i>)	1.538 (7)	C(4 <i>B</i>)—C(18 <i>B</i>)	1.543 (6)
C(5 <i>A</i>)—C(10 <i>A</i>)	1.542 (6)	C(4 <i>B</i>)—C(19 <i>B</i>)	1.524 (5)
C(6 <i>A</i>)—C(7 <i>A</i>)	1.508 (7)	C(5 <i>B</i>)—C(6 <i>B</i>)	1.500 (5)
C(7 <i>A</i>)—C(8 <i>A</i>)	1.539 (6)	C(5 <i>B</i>)—C(10 <i>B</i>)	1.337 (4)
C(8 <i>A</i>)—C(9 <i>A</i>)	1.528 (5)	C(6 <i>B</i>)—C(7 <i>B</i>)	1.508 (6)
C(8 <i>A</i>)—C(14 <i>A</i>)	1.548 (5)	C(7 <i>B</i>)—C(8 <i>B</i>)	1.510 (5)
C(8 <i>A</i>)—C(15 <i>A</i>)	1.534 (5)	C(8 <i>B</i>)—C(9 <i>B</i>)	1.511 (5)
C(9 <i>A</i>)—C(10 <i>A</i>)	1.550 (5)	C(8 <i>B</i>)—C(14 <i>B</i>)	1.562 (5)
C(9 <i>A</i>)—C(11 <i>A</i>)	1.554 (5)	C(8 <i>B</i>)—C(15 <i>B</i>)	1.542 (4)
C(10 <i>A</i>)—C(20 <i>A</i>)	1.555 (5)	C(9 <i>B</i>)—C(10 <i>B</i>)	1.477 (5)
C(11 <i>A</i>)—C(12 <i>A</i>)	1.531 (5)	C(9 <i>B</i>)—C(11 <i>B</i>)	1.326 (5)
C(12 <i>A</i>)—C(13 <i>A</i>)	1.542 (5)	C(11 <i>B</i>)—C(12 <i>B</i>)	1.480 (5)
C(12 <i>A</i>)—C(16 <i>A</i>)	1.554 (5)	C(12 <i>B</i>)—C(13 <i>B</i>)	1.523 (6)
C(13 <i>A</i>)—C(14 <i>A</i>)	1.548 (6)	C(12 <i>B</i>)—C(16 <i>B</i>)	1.522 (5)
C(13 <i>A</i>)—O(<i>A</i>)	1.435 (5)	C(13 <i>B</i>)—C(14 <i>B</i>)	1.508 (6)
C(14 <i>A</i>)—C(20 <i>A</i>)	1.563 (5)	C(13 <i>B</i>)—C(16 <i>B</i>)	1.501 (5)
C(15 <i>A</i>)—C(16 <i>A</i>)	1.511 (6)	C(15 <i>B</i>)—C(16 <i>B</i>)	1.500 (5)
C(16 <i>A</i>)—C(17 <i>A</i>)	1.522 (5)	C(15 <i>B</i>)—O(<i>B</i>)	1.417 (4)
C(16 <i>A</i>)—O(<i>B</i>)	1.452 (4)	C(16 <i>B</i>)—C(17 <i>B</i>)	1.495 (5)
C(17 <i>A</i>)—C(17 <i>B</i>)	1.539 (7)	C(19 <i>B</i>)—N(<i>B</i>)	1.463 (5)
C(19 <i>A</i>)—N(<i>A</i>)	1.457 (7)	C(20 <i>B</i>)—N(<i>B</i>)	1.459 (5)
C(20 <i>A</i>)—N(<i>A</i>)	1.467 (6)	C(21 <i>B</i>)—N(<i>B</i>)	1.456 (6)
C(21 <i>A</i>)—N(<i>A</i>)	1.470 (6)		

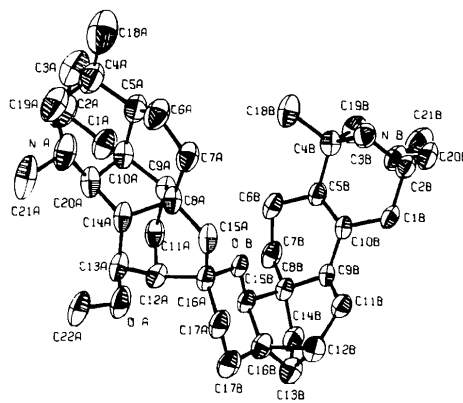


Fig. 1. A three-dimensional 50% probability thermal-ellipsoid plot (Johnson, 1971) of staphisine. The numbering scheme corresponds to that used in Tables 2–4.

is *cis* and it joins unit (*A*) in a spiro junction at C(16*A*). The ring is in the chair conformation with C(8*B*) equatorial and C(12*B*) axial. This conformation keeps the two units of the molecule well separated so that, excluding the atoms of the central ring, there are no contacts between the two units less than 4.0 \AA . The overall conformation of the molecule can be viewed in Fig. 1 (*ORTEP* II; Johnson, 1971) and detailed information about the conformations of the individual rings can be found in Table 5. It should be noted that

Table 4. Bond angles ($^{\circ}$) with *e.s.d.*'s in parentheses

C(2A)–C(1A)–C(10A)	114.2 (4)	C(5A)–C(10A)–C(20A)	108.0 (3)	C(13A)–O(A)–C(22A)	114.0 (3)	C(1B)–C(10B)–C(9B)	116.6 (3)
C(1A)–C(2A)–C(3A)	110.5 (4)	C(9A)–C(10A)–C(20A)	101.2 (3)	C(2B)–C(1B)–C(10B)	114.4 (3)	C(5B)–C(10B)–C(9B)	121.0 (3)
C(2A)–C(3A)–C(4A)	112.1 (5)	C(9A)–C(11A)–C(12A)	111.7 (3)	C(1B)–C(2B)–C(3B)	108.4 (3)	C(9B)–C(11B)–C(12B)	117.4 (3)
C(3A)–C(4A)–C(5A)	109.9 (4)	C(11A)–C(12A)–C(13A)	104.4 (3)	C(1B)–C(2B)–C(20B)	114.2 (3)	C(11B)–C(12B)–C(13B)	119.7 (3)
C(3A)–C(4A)–C(18A)	109.3 (5)	C(11A)–C(12A)–C(16A)	107.9 (3)	C(3B)–C(2B)–C(20B)	109.7 (3)	C(11B)–C(12B)–C(16B)	118.5 (3)
C(3A)–C(4A)–C(19A)	109.1 (4)	C(13A)–C(12A)–C(16A)	112.5 (3)	C(2B)–C(3B)–C(4B)	108.4 (3)	C(13B)–C(12B)–C(16B)	59.1 (2)
C(5A)–C(4A)–C(18A)	110.0 (4)	C(12A)–C(13A)–C(14A)	110.5 (3)	C(3B)–C(4B)–C(5B)	109.6 (3)	C(12B)–C(13B)–C(14B)	111.2 (3)
C(5A)–C(4A)–C(19A)	107.9 (4)	C(12A)–C(13A)–O(A)	109.4 (3)	C(3B)–C(4B)–C(18B)	108.2 (3)	C(12B)–C(13B)–C(16B)	60.5 (2)
C(18A)–C(4A)–C(19A)	110.7 (5)	C(14A)–C(13A)–O(A)	114.1 (3)	C(3B)–C(4B)–C(19B)	107.4 (3)	C(14B)–C(13B)–C(16B)	106.6 (3)
C(4A)–C(5A)–C(6A)	111.1 (4)	C(8A)–C(14A)–C(13A)	107.3 (3)	C(5B)–C(4B)–C(18B)	112.4 (3)	C(8B)–C(14B)–C(13B)	104.4 (3)
C(4A)–C(5A)–C(10A)	108.7 (3)	C(8A)–C(14A)–C(20A)	105.0 (3)	C(5B)–C(4B)–C(19B)	109.9 (3)	C(8B)–C(15B)–C(16B)	104.6 (3)
C(6A)–C(5A)–C(10A)	113.6 (4)	C(13A)–C(14A)–C(20A)	112.3 (3)	C(18B)–C(4B)–C(19B)	109.3 (3)	C(8B)–C(15B)–O(B)	112.8 (3)
C(5A)–C(6A)–C(7A)	113.2 (4)	C(8A)–C(15A)–C(16A)	113.4 (3)	C(4B)–C(5B)–C(6B)	117.0 (3)	C(16B)–C(15B)–O(B)	112.2 (3)
C(6A)–C(7A)–C(8A)	116.6 (3)	C(12A)–C(16A)–C(15A)	105.7 (3)	C(4B)–C(5B)–C(10B)	121.8 (3)	C(12B)–C(16B)–C(13B)	60.5 (3)
C(7A)–C(8A)–C(9A)	110.2 (3)	C(12A)–C(16A)–C(17A)	116.2 (3)	C(6B)–C(5B)–C(10B)	121.2 (3)	C(12B)–C(16B)–C(15B)	113.2 (3)
C(7A)–C(8A)–C(14A)	115.5 (3)	C(12A)–C(16A)–O(B)	109.0 (3)	C(5B)–C(6B)–C(7B)	112.4 (3)	C(12B)–C(16B)–C(17B)	122.2 (3)
C(7A)–C(8A)–C(15A)	107.2 (3)	C(15A)–C(16A)–C(17A)	111.7 (3)	C(6B)–C(7B)–C(8B)	112.2 (3)	C(13B)–C(16B)–C(15B)	106.6 (3)
C(9A)–C(8A)–C(14A)	97.5 (3)	C(15A)–C(16A)–O(B)	103.9 (3)	C(7B)–C(8B)–C(9B)	113.2 (3)	C(13B)–C(16B)–C(17B)	131.3 (4)
C(9A)–C(8A)–C(15A)	115.4 (3)	C(17A)–C(16A)–O(B)	109.6 (3)	C(7B)–C(8B)–C(14B)	112.0 (3)	C(15B)–C(16B)–C(17B)	113.1 (3)
C(14A)–C(8A)–C(15A)	111.1 (3)	C(16A)–C(17A)–C(17B)	115.3 (3)	C(7B)–C(8B)–C(15B)	115.8 (3)	C(17A)–C(17B)–C(16B)	106.7 (3)
C(8A)–C(9A)–C(10A)	101.7 (3)	C(4A)–C(19A)–N(A)	117.1 (4)	C(9B)–C(8B)–C(14B)	108.2 (3)	C(4B)–C(19B)–N(B)	111.8 (3)
C(8A)–C(9A)–C(11A)	108.2 (3)	C(10A)–C(20A)–C(14A)	104.8 (3)	C(9B)–C(8B)–C(15B)	107.5 (3)	C(2B)–C(20B)–N(B)	113.9 (3)
C(10A)–C(9A)–C(11A)	112.4 (3)	C(10A)–C(20A)–N(A)	113.6 (3)	C(14B)–C(8B)–C(15B)	99.1 (3)	C(19B)–N(B)–C(20B)	111.9 (3)
C(1A)–C(10A)–C(5A)	108.8 (4)	C(14A)–C(20A)–N(A)	111.3 (3)	C(8B)–C(9B)–C(10B)	118.5 (3)	C(19B)–N(B)–C(21B)	111.0 (3)
C(1A)–C(10A)–C(9A)	111.3 (3)	C(19A)–N(A)–C(20A)	119.4 (4)	C(8B)–C(9B)–C(11B)	115.0 (3)	C(20B)–N(B)–C(21B)	109.3 (3)
C(1A)–C(10A)–C(20A)	115.7 (3)	C(19A)–N(A)–C(21A)	113.4 (4)	C(10B)–C(9B)–C(11B)	125.9 (3)	C(16A)–O(B)–C(15B)	113.1 (2)
C(5A)–C(10A)–C(9A)	111.6 (3)	C(20A)–N(A)–C(21A)	110.4 (4)	C(1B)–C(10B)–C(5B)	122.2 (3)		

Table 5. Selected torsion angles ($^{\circ}$)

	Unit (A)	Unit (B)		Unit (A)	Unit (B)
Ring A			Ring C/D		
C(1)–C(2)–C(3)–C(4)	–53.8 (5)	–66.7 (4)	C(8)–C(9)–C(11)–C(12)	–3.0 (3)	–3.2 (5)
C(2)–C(3)–C(4)–C(5)	58.8 (5)	57.2 (4)	C(9)–C(11)–C(12)–C(16)	–58.2 (4)	–32.7 (5)
C(3)–C(4)–C(5)–C(10)	–60.5 (5)	–21.5 (4)	C(11)–C(12)–C(16)–C(15)	71.0 (3)	12.8 (5)
C(4)–C(5)–C(10)–C(1)	58.1 (4)	–5.0 (5)	C(12)–C(16)–C(15)–C(8)	–21.4 (4)	36.2 (4)
C(5)–C(10)–C(1)–C(2)	–56.0 (4)	–4.3 (5)	C(16)–C(15)–C(8)–C(9)	–40.5 (4)	–71.0 (3)
C(10)–C(1)–C(2)–C(3)	53.3 (5)	39.9 (4)	C(15)–C(8)–C(9)–C(11)	53.2 (3)	55.8 (4)
Ring B			Ring E		
C(5)–C(6)–C(7)–C(8)	–36.0 (5)	51.3 (4)	C(4)–C(5)–C(10)–C(20)	–68.2 (4)	
C(6)–C(7)–C(8)–C(9)	54.6 (4)	–45.3 (4)	C(5)–C(10)–C(20)–N	23.7 (4)	
C(7)–C(8)–C(9)–C(10)	–66.7 (3)	12.8 (4)	C(10)–C(20)–N–C(19)	28.7 (5)	
C(8)–C(9)–C(10)–C(5)	68.3 (4)	15.6 (5)	C(20)–N–C(19)–C(4)	–39.0 (6)	
C(9)–C(10)–C(5)–C(6)	–54.4 (4)	–9.6 (5)	N–C(19)–C(4)–C(5)	–6.2 (6)	
C(10)–C(5)–C(6)–C(7)	35.4 (5)	–24.2 (4)	C(19)–C(4)–C(5)–C(10)	58.3 (5)	
Ring C			C(2)–C(3)–C(4)–C(19)		–62.1 (4)
C(8)–C(9)–C(11)–C(12)	–3.0 (3)	–3.2 (5)	C(3)–C(4)–C(19)–N		60.6 (4)
C(9)–C(11)–C(12)–C(13)	61.7 (3)	36.0 (5)	C(4)–C(19)–N–C(20)		–55.3 (4)
C(11)–C(12)–C(13)–C(14)	–47.8 (4)	–9.8 (5)	C(19)–N–C(20)–C(2)		51.5 (4)
C(12)–C(13)–C(14)–C(8)	–20.2 (4)	–40.0 (4)	N–C(20)–C(2)–C(3)		–53.8 (4)
C(13)–C(14)–C(8)–C(9)	78.6 (3)	72.0 (3)	C(20)–C(2)–C(3)–C(4)		58.6 (4)
C(14)–C(8)–C(9)–C(11)	–64.4 (3)	–50.2 (4)			
Ring D			Ring F		
C(12)–C(16)–C(15)–C(8)	–21.4 (4)	36.2 (4)	C(8)–C(9)–C(10)–C(20)	–46.4 (3)	
C(16)–C(15)–C(8)–C(14)	69.3 (4)	41.4 (3)	C(9)–C(10)–C(20)–C(14)	19.4 (4)	
C(15)–C(8)–C(14)–C(13)	–42.4 (4)	–39.8 (3)	C(10)–C(20)–C(14)–C(8)	13.4 (4)	
C(8)–C(14)–C(13)–C(12)	–20.2 (4)	–40.0 (4)	C(20)–C(14)–C(8)–C(9)	–41.1 (3)	
C(14)–C(13)–C(12)–C(16)	68.9 (4)	97.6 (3)	C(14)–C(8)–C(9)–C(10)	54.0 (3)	
C(13)–C(12)–C(16)–C(15)	–43.5 (4)	–96.6 (3)			
			Central ring		
			C(16A)–C(17A)–C(17B)–C(16B)	50.3 (4)	
			C(17A)–C(17B)–C(16B)–C(15B)	–51.6 (4)	
			C(17B)–C(16B)–C(15B)–O(B)	58.0 (4)	
			C(16B)–C(15B)–O(B)–C(16A)	–58.5 (3)	
			C(15B)–O(B)–C(16A)–C(17A)	54.6 (3)	
			O(B)–C(16A)–C(17A)–C(17B)	–52.0 (4)	

the C(20)–C(14) bond, not present in atisine itself, forces ring *E* of unit (*A*) into a boat conformation. Also, the *C* and *D* rings of unit (*A*) have slightly different conformations from those in atisium chloride and dihydroatisine, neither of which has a C(20)–C(14) bond (Pelletier, DeCamp & Mody, 1978). The *C*–*D* ring fragments of the latter two structures have nearly the ideal conformation for bicyclo[2.2.2]octane, whereas in unit (*A*) of staphisine the dihedral angles for this fragment deviate from their ideal values of 0, 60, or -60° by an average of 11.5° .

Fractional coordinates and temperature factors, bond distances, bond angles and torsion angles for the non-hydrogen atoms are listed in Tables 2, 3, 4, and 5. The anisotropic thermal parameters for the temperature factor exponentials defined by $T = -2\pi^2 \sum_i \sum_j U_{ij} \times h_i h_j a_i^* a_j^*$ are available.† None of the temperature factor coefficients was nonpositive-definite. The thermal parameters varied from a maximum of $0.197(8) \text{ \AA}^2$ for U_{11} of C(18*A*) to a minimum of $0.023(1) \text{ \AA}^2$ for U_{22} of C(9*B*). The U 's reported in Table 2 are the isotropic temperature factors equivalent to the components of the anisotropic temperature factor matrices, U (Hamilton, 1959).

The absolute configuration of staphisine was not determined from the X-ray data. The fractional coordinates reported correspond to the absolute configuration of atisine, but no relationship between the

two compounds is claimed. Intramolecular bond distances and angles include no remarkable values and there are no significantly short intermolecular distances.

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† Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35538 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of a Psychoactive Agent: 7-Chloro-3-hydroxy-1-methyl-5-phenyl-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one (Temazepam)

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Abstract

The structure of temazepam was solved by direct methods and then refined to $R = 0.057$ ($R_w = 0.040$) for 5108 intensities collected on a diffractometer. Crystals of $C_{16}H_{13}ClN_2O_2$ are monoclinic, space group

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$P2_1/c$, with $a = 19.528(5)$, $b = 11.328(3)$, $c = 20.231(4) \text{ \AA}$, $\beta = 107.0(1)^\circ$ and twelve molecules in the unit cell; $D_m = 1.40$ (by flotation), $D_x = 1.400 \text{ Mg m}^{-3}$, $F(000) = 1872$. There are no distinct hydrogen bonds in the crystal as the shortest $H \cdots O$ distance is 2.05 \AA . The seven-membered ring is in a boat

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