N3	0.0837 (8)	0.4111 (6)	0.4459 (6)	3.0 (3)
O1	0.0929 (6)	0.4130 (5)	0.6880 (5)	3.4 (3)
O*W*	0.0736 (9)	0.1868 (9)	0.3648 (9)	8.2 (5)

Table 2. *Bond distances* (Å) *and angles* (°)

C11—C12	1.43 (3)	C31—C32	1.35 (3)
C12—C13	1.36 (3)	C32—C33	1.38 (3)
C13—C14	1.39 (3)	C33—C34	1.39 (3)
C14—C15	1.43 (3)	C34—C35	1.39 (3)
C15—C16	1.32 (3)	C35—C36	1.39 (3)
C11—C16	1.30 (3)	C31—C36	1.33 (3)
C1—C13	1.49 (3)	C3—C33	1.58 (3)
N1—C14	1.44 (3)	N3—C34	1.45 (3)
C11—Br1	1.92 (2)	C31—Br3	1.93 (3)
C21—C22	1.39 (3)	C1—N3	1.47 (3)
C22—C23	1.41 (3)	C1—O1	1.44 (3)
C23—C24	1.35 (3)	O1—C4	1.46 (3)
C24—C25	1.45 (3)	C4—C5	1.47 (3)
C25—C26	1.36 (3)	C2—N1	1.45 (3)
C21—C26	1.35 (3)	C2—N3	1.46 (3)
C2—C23	1.53 (3)	C3—N1	1.45 (3)
N2—C24	1.41 (3)	C3—N2	1.43 (3)
C21—Br2	1.95 (2)		
Br1—C11—C16	119 (2)	C31—C36—C35	119 (2)
Br1—C11—C12	118 (1)	C32—C31—C36	125 (2)
Br2—C21—C22	116 (2)	C32—C33—C3	121 (2)
Br2—C21—C26	119 (2)	C33—C32—C31	118 (2)
Br3—C31—C32	118 (2)	C33—C34—N3	120 (2)
Br3—C31—C36	117 (2)	C34—C33—C32	120 (2)
C11—C16—C15	121 (2)	C34—N3—C2	112 (2)
C12—C13—C1	119 (2)	C34—N3—C1	112 (2)
C12—C11—C16	123 (2)	C35—C34—C33	119 (2)
C13—C14—N1	121 (2)	C35—C34—N3	120 (2)
C13—C1—O1	110 (2)	C36—C35—C34	119 (2)
C13—C12—C11	117 (2)	C1—C13—C14	120 (2)
C14—N1—C2	111 (2)	C1—O1—C4	114 (2)
C14—C13—C12	121 (2)	C2—C23—C24	121 (2)
C15—C14—C13	118 (2)	C2—C23—C22	117 (2)
C15—C14—N1	120 (2)	C2—N3—C1	108 (1)
C16—C15—C14	120 (2)	C3—C33—C34	119 (2)
C21—C26—C25	120 (3)	C3—N1—C2	107 (2)
C22—C21—C26	125 (2)	C3—N1—C14	116 (2)
C23—C22—C21	115 (2)	N1—C2—C23	109 (2)
C23—C2—N3	113 (2)	N1—C2—N3	111 (2)
C23—C24—N2	120 (2)	N1—C3—C33	111 (2)
C24—C23—C22	121 (2)	N2—C3—N1	110 (2)
C24—N2—C3	113 (2)	N2—C3—C33	112 (2)
C25—C24—C23	121 (2)	N2—C24—C25	119 (2)
C26—C25—C24	117 (2)	N3—C1—C13	113 (2)
O1—C4—C5	107 (2)	N3—C1—O1	109 (2)

Programs used were *SHELX*76 (Sheldrick, 1976) and *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters for the Br atoms and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71452 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1063]

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Structure of Neostrychnine. An Enamine with a Bridgehead Nitrogen which Undergoes Efficient Chemical Reaction with Singlet Oxygen

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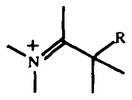
Abstract

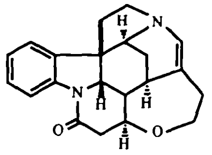
Neostrychnine, 20,21-didehydro-21,22-dihydrostrychnidin-10-one, $C_{21}H_{22}N_2O_2$, contains an alicyclic enamine unit in which the N atom is located at a bridgehead, a fact of critical importance to an understanding of the manner in which it reacts with potential electrophiles, including singlet oxygen, $O_2(^1\Delta_g)$. The X-ray structure shows that the steric constraints within the σ framework demand a high degree of pyramidalization of the N atom, which is independent of the fact that this atom is part of an enamine system. These data support the conclusion that the formation of an immonium species with a double bond at the N atom is likely to be highly unfavourable.

Comment

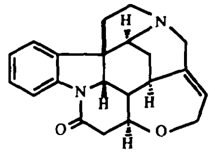
The mechanism of chemical reaction of singlet oxygen, $O_2(^1\Delta_g)$, with electron-rich double bonds, including those of enamines, to give dioxetanes has been a subject of considerable discussion (Yamaguchi, 1985). Trapping experiments (Jefford, Kohmoto, Boukouvalas & Burger, 1983, and references therein; Saito, Nakagawa, Kuo, Obata & Matsuura, 1985, and references therein) have been interpreted as conclusive evidence for the intermediacy of zwitterionic species of type (1*a*).



(1*a*) *R* = O—O
(1*b*) *R* = H



(2)



(3)

The long-known molecule neostrychnine (2) (Chakravarti & Robinson, 1947), an isomer of strychnine (3) of known absolute stereochemistry (Peierdeman, 1956), provides a potential test of these claims since its very low pK_a suggests that the immonium species (1*b*) is energetically unfavoured, in agreement with the requirement to accommodate a bridgehead double bond (Prelog & Hafliger, 1949; Prelog, Barman & Zimmermann, 1949). Therefore, reaction with $O_2(^1\Delta_g)$ *via* (1*a*) should also be unfavoured. Experiment, however, has shown that chemical reaction of (2) with $O_2(^1\Delta_g)$ is extremely efficient, proceeding with a rate constant typical of a standard sterically unconstrained enamine and thus providing evidence that the rate-determining step does not involve a species corresponding to (1*a*) (Curtis, Gorman & Prescott, 1988).

In this paper we report the structure determination of (2). This shows that the alicyclic N atom in this molecule exhibits a high degree of pyramidalization which is essentially identical to that of strychnine (3) (Glover, Gould & Walkinshaw, 1985). This implies that the hybridization of the N atom in neostrychnine (2) is a consequence of σ-framework constraints within the polycyclic structure as a whole, and supports the contention that an immonium species of type (1) must be highly unfavourable.

Crystalline (2) was prepared by refluxing strychnine with Raney Nickel in xylene (Chakravarti & Robinson, 1947). Fig. 1 shows a *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule together with the numbering system used. We have compared the hybridization of the aliphatic N atoms in (2) and (3) by computing (*a*) the vertical distance of each N atom from the plane of the three C atoms to which it is bonded and (*b*) the sum of the three bond angles centred at each N atom. The values are extremely similar [0.44 Å and 334.4° for (2) from this work, 0.44 Å and 335.0° for (3) using coordinates from Glover, Gould & Walkinshaw (1985)].

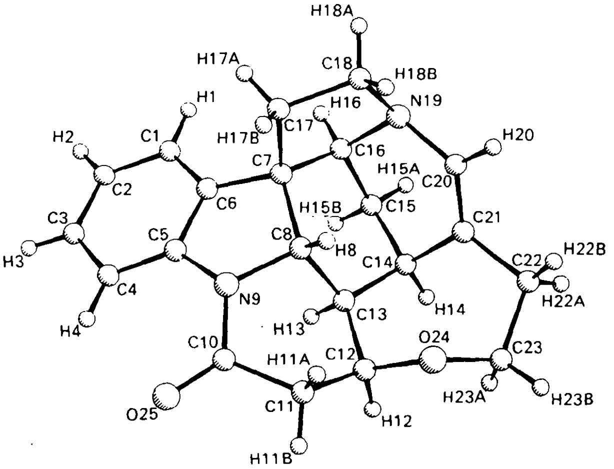


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of neostrychnine (2) showing the numbering scheme used in the tables.

Experimental

The compound was obtained by treatment of strychnine with Raney nickel in xylene (Chakravarti & Robinson, 1947), followed by dry-column chromatography on silica gel with acetone/hexane mixtures and recrystallization twice from absolute ethanol; m.p. 500-502.5 K (Prescott, 1990).

Crystal data

$C_{21}H_{22}N_2O_2$
M_r = 334.42
Orthorhombic
$P2_12_12_1$
a = 7.974 (4) Å
b = 11.960 (4) Å
c = 16.482 (8) Å
V = 1572 (2) Å^3
Z = 4
D_x = 1.413 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 47 reflections
θ = 6.3-11.9°
μ = 0.085 mm^{-1}
T = 294 K
Tabular
0.4 × 0.4 × 0.18 mm
Colourless

Data collection

Nicolet diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2578 measured reflections
2201 independent reflections
1458 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.06

$\theta_{\rm max}$ = 27.5°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 200 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.068$
$wR = 0.044$
$S = 1.787$
1458 reflections
226 parameters
H-atom parameters not refined

$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
C1	0.335 (1)	0.3811 (6)	0.3905 (4)	3.0 (4)
C2	0.216 (1)	0.3998 (6)	0.4501 (4)	3.9 (5)
C3	0.091 (1)	0.3260 (8)	0.4657 (4)	3.6 (5)
C4	0.076 (1)	0.2263 (6)	0.4209 (4)	3.6 (5)
C5	0.194 (1)	0.2095 (6)	0.3619 (4)	2.9 (5)
C6	0.321 (1)	0.2847 (6)	0.3446 (4)	2.5 (4)
C7	0.4328 (9)	0.2400 (5)	0.2778 (4)	2.3 (4)
C8	0.3232 (8)	0.1478 (5)	0.2408 (4)	2.4 (4)
N9	0.2049 (7)	0.1162 (5)	0.3068 (3)	2.8 (3)
C10	0.075 (1)	0.0442 (6)	0.2895 (4)	3.2 (5)
C11	0.090 (1)	−0.0089 (5)	0.2056 (4)	3.3 (4)
C12	0.132 (1)	0.0714 (6)	0.1369 (4)	3.1 (4)
C13	0.2135 (8)	0.1806 (5)	0.1680 (4)	2.4 (4)
C14	0.304 (1)	0.2530 (6)	0.1054 (4)	2.7 (4)
C15	0.368 (1)	0.3567 (5)	0.1501 (4)	2.6 (4)
C16	0.497 (1)	0.3227 (6)	0.2135 (4)	2.8 (4)
C17	0.600 (1)	0.1964 (6)	0.3118 (4)	3.1 (4)
C18	0.7245 (8)	0.2025 (6)	0.2406 (4)	3.3 (4)
N19	0.6401 (8)	0.2656 (5)	0.1751 (3)	2.9 (3)
C20	0.599 (1)	0.1982 (6)	0.1064 (4)	3.1 (5)
C21	0.453 (1)	0.1928 (6)	0.0701 (4)	2.7 (4)
C22	0.423 (1)	0.1196 (7)	−0.0036 (4)	3.6 (4)
C23	0.260 (1)	0.0548 (6)	0.0044 (5)	4.4 (5)
O24	0.2415 (6)	0.0080 (4)	0.0846 (3)	3.6 (3)
O25	−0.0379 (6)	0.0256 (4)	0.3361 (3)	4.2 (3)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.385 (9)	C11—C12	1.525 (8)
C1—C6	1.384 (8)	C12—C13	1.545 (8)
C2—C3	1.36 (1)	C12—O24	1.441 (7)
C3—C4	1.408 (9)	C13—C14	1.530 (8)
C4—C5	1.369 (9)	C14—C15	1.529 (8)
C5—C6	1.383 (9)	C14—C21	1.506 (9)
C5—N9	1.441 (8)	C15—C16	1.521 (9)
C6—C7	1.515 (8)	C16—N19	1.474 (8)
C7—C8	1.533 (8)	C17—C18	1.540 (9)
C7—C16	1.537 (8)	C18—N19	1.479 (8)
C7—C17	1.538 (9)	N19—C20	1.427 (8)
C8—N9	1.489 (7)	C20—C21	1.311 (9)
C8—C13	1.536 (8)	C21—C22	1.517 (9)
N9—C10	1.375 (8)	C22—C23	1.51 (1)
C10—C11	1.525 (8)	C23—O24	1.444 (8)
C10—O25	1.206 (8)		
C2—C1—C6	117.8 (7)	C11—C12—C13	112.3 (6)
C1—C2—C3	122.3 (7)	C11—C12—O24	104.3 (6)
C2—C3—C4	120.9 (7)	C13—C12—O24	112.9 (6)
C3—C4—C5	116.0 (7)	C8—C13—C12	106.5 (5)
C4—C5—C6	123.7 (7)	C8—C13—C14	113.6 (6)
C4—C5—N9	127.1 (7)	C12—C13—C14	117.0 (6)
C6—C5—N9	109.2 (7)	C13—C14—C15	107.0 (5)
C1—C6—C5	119.3 (7)	C13—C14—C21	111.3 (6)
C1—C6—C7	130.0 (7)	C15—C14—C21	108.2 (6)
C5—C6—C7	110.6 (6)	C14—C15—C16	109.8 (6)
C6—C7—C8	101.9 (6)	C7—C16—C15	114.9 (6)
C6—C7—C16	118.1 (6)	C7—C16—N19	104.8 (6)
C6—C7—C17	111.5 (6)	C15—C16—N19	110.6 (5)
C8—C7—C16	112.2 (5)	C7—C17—C18	105.3 (5)
C8—C7—C17	113.2 (6)	C17—C18—N19	106.7 (6)
C16—C7—C17	100.4 (6)	C16—N19—C18	105.9 (5)
C7—C8—N9	104.7 (5)	C16—N19—C20	115.3 (6)
C7—C8—C13	116.9 (6)	C18—N19—C20	113.2 (6)
N9—C8—C13	105.9 (5)	N19—C20—C21	126.3 (7)
C5—N9—C8	107.6 (5)	C14—C21—C20	120.1 (7)
C5—N9—C10	124.7 (6)	C14—C21—C22	117.4 (6)
C8—N9—C10	119.0 (6)	C20—C21—C22	122.4 (7)
N9—C10—C11	113.1 (7)	C21—C22—C23	111.2 (6)
N9—C10—O25	123.1 (7)	C22—C23—O24	111.6 (7)
C11—C10—O25	123.7 (8)	C12—O24—C23	114.0 (5)
C10—C11—C12	115.3 (6)		

The known handedness was chosen for the absolute structure. Refinement of the enantiomer using anomalous-dispersion coefficients gave only a slightly higher agreement factor: 0.0683 compared with 0.0682. Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964). H atoms were included at calculated positions (C—H = 0.95 Å) and not refined. Computer programs used were *DIFABS* (Walker & Stuart, 1983), *SHELX*86 (Sheldrick, 1985), *TEXSAN* (Molecular Structure Corporation, 1985) and *PLUTO* (Motherwell & Clegg, 1978).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71580 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1064]

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Structural Investigations of 1,2,3,4-Tetrahydrocarbazole Derivatives. I. 2,3-Dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one and 1,2,3,4-Tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane

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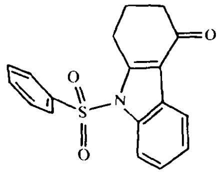
Abstract

Rings *A* and *B* of the title compounds, $C_{18}H_{15}NO_3S$ (1) and $C_{14}H_{15}NS_2$ (2), are planar while the hydrogenated *C* rings are not. The rings in the tetrahydrocarbazole skeleton are twisted with respect to each other.

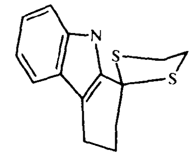
Comment

The title compounds have tricyclic ring systems with the rings named as *A*, *B* and *C* as in the strychnos type of indol alkaloids (Bosch & Bonjoch, 1988). Synthesis of these compounds is currently being studied using the title compounds as starting materials (Götz, Bats & Fritz, 1986; Patır & Fritz, 1990). When positions 2 or 3 of the title compounds were substituted by appropriate substituents, synthesis of the dasycarbidone skeleton was accomplished (Magnus, Sear, Kim & Vicker, 1992). The possibility of synthesizing the indol type of alkaloids by substitution at either position 1 or other positions is currently under investigation (Patır & Götz, 1993).

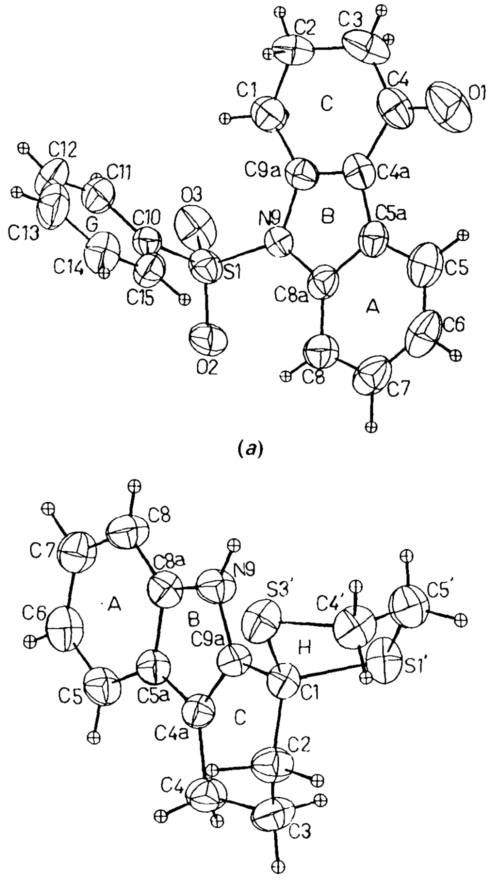
Compound (1) was prepared from tetrabutylammonium hydrogensulfate, benzoylsulfonyl chloride and 1,2,3,4-tetrahydrocarbazole-4-one by the method of Volker (1979) (see also Patır, 1991). Compound (2) was prepared from 1,2,3,4-tetrahydrocarbazole-1-one and ethanedithiol using $ZnCl_2$ as a catalyst (Patır & Götz, 1993). Perspective views of compounds (1) and (2) are shown in Fig. 1 and the crystal packings are presented in Fig. 2.



(1)



(2)



(*a*)

(*b*)

Fig. 1. *SNOOPI* (Davies, 1983) drawings of (*a*) compound (1) and (*b*) compound (2) with the atom-numbering schemes. The thermal ellipsoids are drawn at the 50% probability level.