

Fig. 2. Packing of molecules in the unit cell (viewed down **b**). Dotted lines indicate alternate positions. Dashed lines indicate the three intramolecular short contacts.

Bond lengths and angles, given in Table 2, are mostly within the range of standard values (Sutton, 1965). However, rather large differences are seen for the bonds C(3C)—C(4C), C(4C)—C(5C) and C(6C)—C(1C) of the ring C, but these are presumably due to the larger positional errors near the disordered region where the two alternate configurations around the S atom have to be accommodated.

Fig. 2 (a projection along **b**) shows the packing of the molecules in the unit cell. S=O(1') bonds are shown by dotted lines. Short contacts C(6)···O(1) [3·122 (4)], C(6C)···O(1) [2·839 (6)] and C(6A)—O(5) [2·940 (2) Å] are shown by dashed lines. These short

contacts may be responsible for the differences in the torsion angles around the junction between the phenyls and the pyrazone: C(5)—N(1)—C(1A)—C(2A) is $-121.7 (4)$ and C(3)—N(2)—C(1B)—C(6B) $88.6 (4)^\circ$, a difference of 33° . As a result, phenyl ring A makes an angle of $46.3 (5)^\circ$ and ring B an angle of $110.4 (5)^\circ$ with the pyrazone ring. There are some intermolecular short contacts such as C(5A)···O(1) and C(6A)···O(5) with distances of $3.221 (2)$ and $3.203 (3)$ Å respectively, which may be responsible for loosely holding the molecules in the crystal.

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5,11-Dimethyl-6H-pyrido[4,3-b]carbazole 2-Oxide Trihydrate (Ellipticine N-Oxide Trihydrate), C₁₇H₁₄N₂O₃·3H₂O

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Abstract. $M_r = 316.4$, monoclinic, $P2_1/c$, $a = 12.229 (3)$, $b = 6.962 (3)$, $c = 18.946 (6)$ Å, $\beta = 106.67 (3)^\circ$, $V = 1545 (1)$ Å³, $Z = 4$, $D_x = 1.360 (1)$, $D_m = 1.35 (1)$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.91$ cm⁻¹, $F(000) = 672$, $T = 295 (1)$ K. Final $R = 0.045$ for 887 observed reflections. This is a new compound from the oxidation of ellipticine with hydrogen peroxide. The structural parameters are, in general, normal and are compared with those in ellipticine and related compounds. The organic molecule, except for the methyl H atoms, is nearly planar with the maximum deviation of any non-H atom

from the best least-squares plane being $0.048 (6)$ Å for a methyl C atom. The three waters of hydration are involved in a hydrogen-bonding network with each other, the N-oxide O, and the H of the NH group. The N-oxide O acts as the acceptor for three water H atoms.

Introduction. Ellipticine, a naturally occurring alkaloid, is known to exhibit antitumor activity *in vitro* because of its ability to intercalate with DNA (Le Pecq, Dat-Xuong, Gosse & Paoletti, 1974). The planar ring system is known to insert between the DNA strands with overlap between the heterocyclic ring system and

the DNA base pairs (Jain, Bhandary & Sobell, 1979). Since the presence of a positive charge on the N(2) atom increases the stability of such complexes (Le Pecq & Paoletti, 1967), the synthesis of the 2(*N*)-oxide was undertaken. The primary goal in this X-ray study was to determine the degree of planarity of the 2(*N*)-oxide ellipticine molecule.

Experimental. Ellipticine *N*-oxide is a new compound prepared by oxidation of the parent heterocycle using *tert*-butyl hydroperoxide in the presence of molybdenum hexacarbonyl (Sheng & Zagacek, 1968) and by deacetylation of 6-acetyl-5,11-dimethylpyrido[4,3-*b*]carbazole 2-oxide employing absolute ethanol in the presence of *p*-toluenesulfonic acid. Crystals obtained from aqueous ethanol [X-ray crystal a prism ($\sim 0.15 \times 0.25 \times 0.40$ mm)]. D_m measured by flotation.

Enraf-Nonius CAD-4 diffractometer, 18 reflections with $20 < 2\theta < 30^\circ$ used for cell parameters, no absorption correction (estimated range $< 2\%$ based on ψ scans), 2904 reflections (range of hkl : h 0 \rightarrow 11, k 0 \rightarrow 6, l $-18\rightarrow$ 17) with $2\theta < 40^\circ$ measured; three standard reflections after every 8000 s of X-ray exposure revealed no significant variation, three orientation check standards after every 200 reflections with recentering of all 18 reflections if any significant angular error; 1445 unique reflections [887 with $F_o > 2\sigma(F_o)$], $R_{int} = 0.041$, structure solved by *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$; H atoms from difference Fourier syntheses and chemical reasonability (not refined), 208 variables (x, y, z , six β 's for all non-H atoms), $R = 0.045$, $wR = 0.053$, $S = 1.42$, $w^{-1} = (\sigma^2_{counting} + 0.05F_o^2)$, max. shift/error = 0.01, no extinction correction, max. $\Delta\rho$ on final difference Fourier map $0.4 \text{ e } \text{\AA}^{-3}$, scattering factors including f' and f'' values from *International Tables for X-ray Crystallography* (1974), computations on PDP 11/34 computer using Enraf-Nonius *SDP* (1981) programs.

Discussion. Final parameters for non-H atoms are in Table 1.* The molecular structure, including the hydrogen bonding with the water molecules, and the atom labeling are given in Fig. 1. Table 2 gives the bond distances and angles. The structure consists of nearly planar ellipticine *N*-oxide molecules linked by hydrogen bonding with the three waters of hydration. Other than the methyl C atoms [0.048 (6) and 0.045 (6) Å], the largest deviations from the best least-squares plane through the 20 non-H atoms of the ellipticine *N*-oxide

molecule are for the atoms in the *N*-oxide ring [e.g. C(3) and C(4), 0.034 (5) and 0.036 (5) Å and C(1), -0.020 (5) Å].

Table 1. Positional parameters and equivalent isotropic temperature factors (\AA^2) with e.s.d.'s in parentheses for ellipticine *N*-oxide

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^*
C(1)	0.7705 (4)	0.3092 (7)	0.1227 (2)	3.7 (1)
N(2)	0.8691 (3)	0.3431 (6)	0.1100 (2)	3.7 (1)
C(3)	0.8769 (4)	0.3564 (8)	0.0398 (3)	4.0 (1)
C(4)	0.7839 (4)	0.3370 (7)	-0.0178 (2)	3.6 (1)
C(5)	0.5772 (4)	0.2783 (7)	-0.0686 (2)	3.1 (1)
N(6)	0.3684 (3)	0.2241 (6)	-0.0993 (2)	3.7 (1)
C(7)	0.1735 (4)	0.1676 (7)	-0.0875 (3)	3.9 (1)
C(8)	0.1135 (4)	0.1452 (8)	-0.0369 (3)	4.4 (1)
C(9)	0.1669 (4)	0.1550 (8)	0.0386 (3)	4.5 (1)
C(10)	0.2829 (4)	0.1835 (7)	0.0649 (2)	4.2 (1)
C(11)	0.5633 (4)	0.2569 (7)	0.0813 (2)	3.0 (1)
C(12)	0.5586 (4)	0.2417 (9)	0.1589 (3)	4.7 (1)
C(13)	0.5820 (4)	0.2827 (9)	-0.1468 (3)	4.7 (1)
C(14)	0.6743 (3)	0.3004 (7)	-0.0085 (2)	3.1 (1)
C(15)	0.4754 (3)	0.2482 (7)	-0.0512 (2)	3.1 (1)
C(16)	0.2909 (4)	0.1969 (7)	-0.0595 (2)	3.4 (1)
C(17)	0.3473 (4)	0.2066 (7)	0.0159 (2)	3.1 (1)
C(18)	0.4683 (3)	0.2376 (7)	0.0226 (2)	2.9 (1)
C(19)	0.6685 (3)	0.2899 (7)	0.0658 (2)	2.9 (1)
O(20)	0.9649 (3)	0.3609 (5)	0.1666 (2)	4.83 (9)
OW(1)	0.1373 (3)	0.8688 (6)	0.6781 (2)	6.2 (1)
OW(2)	0.2763 (3)	0.2080 (6)	0.7438 (2)	6.0 (1)
OW(3)	0.0868 (3)	0.4735 (6)	0.7142 (2)	5.5 (1)

$$* B_{eq} = \frac{1}{3}(a^2 B_{11} + \dots + bc \cos \alpha B_{23} + \dots).$$

Table 2. Bond distances (Å) and angles ($^\circ$) for ellipticine *N*-oxide

Numbers in parentheses are e.s.d.'s in the least-significant digits.

C(1)–N(2)	1.317 (5)	C(7)–C(16)	1.395 (6)
C(1)–C(19)	1.402 (6)	C(8)–C(9)	1.393 (6)
N(2)–C(3)	1.363 (5)	C(9)–C(10)	1.376 (6)
N(2)–O(20)	1.347 (4)	C(10)–C(17)	1.389 (6)
C(3)–C(4)	1.338 (6)	C(11)–C(12)	1.490 (6)
C(4)–C(14)	1.424 (6)	C(11)–C(18)	1.365 (6)
C(5)–C(13)	1.498 (6)	C(11)–C(19)	1.419 (5)
C(5)–C(14)	1.399 (6)	C(14)–C(19)	1.430 (5)
C(5)–C(15)	1.393 (5)	C(15)–C(18)	1.426 (5)
N(6)–C(15)	1.374 (5)	C(16)–C(17)	1.399 (5)
N(6)–C(16)	1.382 (5)	C(17)–C(18)	1.465 (6)
C(7)–C(8)	1.374 (6)		
N(2)–C(1)–C(19)	122.4 (4)	C(4)–C(14)–C(19)	116.4 (4)
C(1)–N(2)–C(3)	120.9 (4)	C(5)–C(14)–C(19)	121.7 (4)
C(1)–N(2)–O(20)	120.2 (4)	C(5)–C(15)–N(6)	127.4 (4)
C(3)–N(2)–O(20)	118.8 (4)	C(5)–C(15)–C(18)	123.4 (4)
N(2)–C(3)–C(4)	120.6 (4)	N(6)–C(15)–C(18)	109.2 (4)
C(3)–C(4)–C(14)	121.7 (4)	N(6)–C(16)–C(7)	127.2 (4)
C(13)–C(5)–C(14)	122.6 (4)	N(6)–C(16)–C(17)	109.6 (4)
C(13)–C(5)–C(15)	121.9 (4)	C(7)–C(16)–C(17)	123.2 (4)
C(14)–C(5)–C(15)	115.5 (4)	C(10)–C(17)–C(16)	118.0 (4)
C(15)–N(6)–C(16)	109.1 (3)	C(10)–C(17)–C(18)	135.4 (4)
C(8)–C(7)–C(16)	116.6 (4)	C(16)–C(17)–C(18)	106.6 (3)
C(7)–C(8)–C(9)	121.6 (4)	C(11)–C(18)–C(15)	121.1 (4)
C(8)–C(9)–C(10)	120.7 (4)	C(11)–C(18)–C(17)	133.4 (4)
C(9)–C(10)–C(17)	119.8 (4)	C(15)–C(18)–C(17)	105.5 (4)
C(12)–C(11)–C(18)	122.2 (4)	C(1)–C(19)–C(11)	121.0 (4)
C(12)–C(11)–C(19)	120.6 (4)	C(1)–C(19)–C(14)	117.9 (4)
C(18)–C(11)–C(19)	117.1 (4)	C(11)–C(19)–C(14)	121.1 (4)
C(4)–C(14)–C(5)	121.8 (4)		

* Lists of structure factors, H-atom parameters, least-squares-plane results, anisotropic thermal parameters and hydrogen-bond parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39567 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

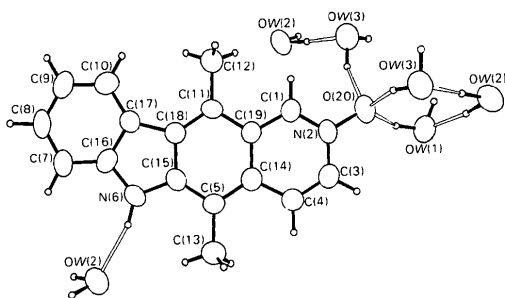


Fig. 1. Perspective view of the ellipticine *N*-oxide molecule showing the atom labeling and the hydrogen bonding with water molecules (open bonds).

Except for a shortening of the C(15)–C(18) and C(3)–C(4) bonds as well as the C(methyl)–C(ring) bonds, the structural parameters compare well with those reported for the parent ellipticine (Courseille, Busetta & Hospital, 1974) and 5,6,11-trimethylpyrido[4,3-*b*]carbazole (Courseille, Busetta & Précigoux, 1981). The N–O bond distance and associated bond angles are comparable with those found for pyridine *N*-oxide (Desiderato & Terry, 1970). However, the N–O distance of 1.347 (4) Å is longer than those found in compounds such as 2-[(hydroxymethoxy)methyl]thio}pyridine 1-oxide [1.319 (5) Å] (Haugwitz, Toeplitz & Gougoutas, 1980), 6-chloro-3-ethoxycarbonyl-2-methylquinoxaline 1,4-dioxide [1.294 (2) and 1.308 (2) Å] (MacDonald & Arora, 1981) and others. The *N*-oxide bond length is apparently highly sensitive to its chemical environment.

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(*E*)-1,2-Bis(2-methoxyphenyl)ethene,* C₁₆H₁₆O₂

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Abstract. $M_r = 240.4$, orthorhombic, *Pbca*, $a = 13.341$ (3), $b = 14.412$ (4), $c = 13.753$ (4) Å, $V = 2644$ (2) Å³, $Z = 8$, $D_x = 1.207$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.73$ cm⁻¹, $F(000) = 1024$, $T = 299$ K, final $R = 0.044$ for 946 observations. The compound was synthesized by reductive coupling of 2-methoxybenzaldehyde. In the crystal, the molecule deviates

While the hydrogen-bond parameters* are normal, their presence indicates that the *N*-oxide should be held strongly to DNA by hydrogen bonding. Moreover if the *N*-oxide carries such waters with it between the strands of DNA, the unwinding angle of the genetic material should be larger than that realized with ellipticine itself thus promoting higher biological activity (Sainsbury, 1979).

* See previous footnote.

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slightly from the planar structure of *2/m* symmetry. One phenyl ring is nearly coplanar with the double bond [dihedral angle 2.7 (3)°], while the other forms a dihedral angle of 15.0 (3)° with it.

Introduction. In the course of our studies utilizing 1,2-bis(2-substituted-phenyl)ethenes as models for intramolecular reactions (Tirado-Rives, Gandour & Fronczek, 1982; Tirado-Rives, Oliver, Fronczek & Gandour, 1984; Fronczek, Oliver & Gandour, 1984),

* Alternative nomenclature: (*E*)-2,2'-dimethoxystilbene.

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