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(−)-(R)-N-[(3,4-Dihydro-2H-1-benzopyran-2-yl)methyl]-N'-(1,4,5,6-tetrahydro-2-pyrimidyl)-1,3-propanediaminium Dibromide†

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Abstract

The crystal structure and absolute configuration of the (−)-enantiomer of the title compound, $C_{17}H_{28}N_4O^{2+}$.-$2Br^-$, have been determined. The absolute configuration is *R*. The bridging chain between the ring moieties is folded with a $-sc/ap/sc/sc/ap/-sc$ conformation. N—H···Br hydrogen bonds form endless chains in the **b** direction.

Comment

Alniditan (R91274), the hydrochloride form of the title compound, (I), interacts primarily with 5-HT_{1D}-serotonergic binding sites and at slightly higher concentrations with the closely related 5-HT_{1A}-serotonergic binding sites. Intravenous and subcutaneous injection of alniditan in patients experiencing moderate to severe migraine pain resulted in a significantly higher response rate than placebo, and this response rate increased with increasing doses.

(I)
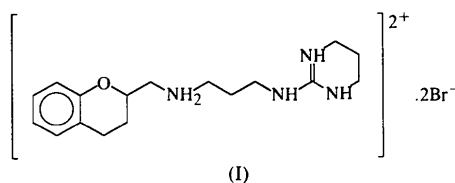
The crystal structure determination of the title compound was undertaken to obtain the absolute configuration of alniditan. Compared to the values given by Allen *et al.* (1987) the bond lengths are normal. The bond angles do not show unexpected features. The double protonation occurs at the basic N atoms N12 and N18 (or N22). This agrees with the less basic properties of N16 through delocalization of its lone pair. The dihydropyran ring adopts a half-chair conformation with a pseudo twofold axis intersecting the C2—C3 bond. The tetrahydropyrimidine ring has an envelope conformation with the flap at C20. The bridging chain between the ring moieties is folded and has a $-sc/ap/sc/sc/ap/-sc$ conformation. The *gauche* conformation between O1 and N12 is stabilized by an intramolecular hydrogen bond. The packing of the molecules results mainly from N—H···Br intermolecular hydrogen bonds which form endless chains in the **b** direction.
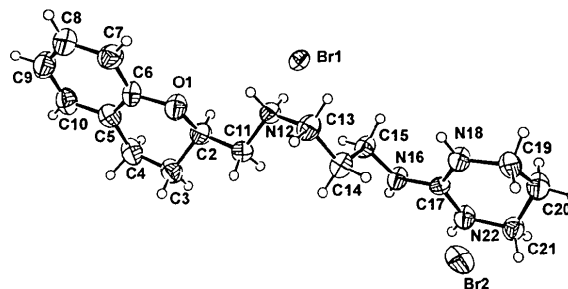

Fig. 1. Perspective view of the title compound with atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Experimental

Crystals of the title compound (Janssen Research Foundation) were grown from a mixture of methanol/ethyl acetate by slow evaporation at room temperature.

Crystal data

$C_{17}H_{28}N_4O^{2+}.2Br^-$
$M_r = 464.26$
Monoclinic
$P2_1$
$a = 7.7033 (2)$ Å
$b = 8.4943 (2)$ Å
$c = 15.4169 (5)$ Å
$\beta = 96.201 (5)°$
$V = 1002.89 (5)$ Å^3
$Z = 2$
$D_x = 1.537$ Mg m^{-3}
$D_m = 1.540$ Mg m^{-3}
D_m measured by flotation in CCl$_4$/n-heptane

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 26 reflections
$\theta = 20–25°$
$\mu = 5.210$ mm^{-1}
$T = 293$ K
Plate
$0.38 \times 0.30 \times 0.05$ mm
Colourless

Data collection

Siemens P4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (XEMP; Siemens, 1989)
  $T_{min} = 0.21$, $T_{max} = 0.77$
5354 measured reflections
2710 independent reflections
2700 observed reflections
  $[I > 2.0\sigma(I)]$

$R_{int} = 0.0398$
$\theta_{max} = 57.16°$
$h = -7 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$
3 standard reflections
  monitored every 100 reflections
  intensity decay: <3.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0333$
$wR(F^2) = 0.0842$
$S = 1.085$
2710 reflections
218 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.8398P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Extinction correction:
  SHELXL93 (Sheldrick, 1993)
Extinction coefficient:
  0.0055 (3)
Atomic scattering factors
  from International Tables
  for X-ray Crystallography
  (1974, Vol. IV) Tables
  2.2B and 2.3.1
Absolute configuration:
  Flack (1983)
Flack parameter = -0.01 (3)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Br1	-0.19971 (6)	0.97130 (5)	0.99501 (3)	0.0580 (2)
Br2	0.2397 (1)	1.74325 (8)	1.29074 (6)	0.0994 (4)
O1	0.2263 (6)	0.7980 (4)	0.8187 (2)	0.062 (1)
C2	0.1918 (6)	0.9613 (6)	0.8336 (3)	0.055 (2)
C3	0.2608 (9)	1.0651 (7)	0.7640 (4)	0.065 (2)
C4	0.1787 (9)	1.0194 (7)	0.6745 (4)	0.072 (2)
C5	0.1663 (7)	0.8446 (7)	0.6628 (4)	0.058 (2)
C6	0.1884 (7)	0.7444 (7)	0.7347 (3)	0.055 (2)
C7	0.1805 (8)	0.5811 (7)	0.7257 (4)	0.064 (2)
C8	0.1439 (9)	0.5172 (8)	0.6423 (5)	0.078 (3)
C9	0.1226 (9)	0.6126 (9)	0.5711 (5)	0.078 (3)
C10	0.1348 (7)	0.7757 (8)	0.5809 (4)	0.067 (2)
C11	0.2770 (7)	0.9957 (7)	0.9227 (3)	0.058 (2)
N12	0.2198 (6)	0.8826 (5)	0.9879 (3)	0.052 (2)
C13	0.3341 (8)	0.8739 (6)	1.0728 (4)	0.059 (2)
C14	0.3640 (7)	1.0328 (6)	1.1172 (4)	0.057 (2)
C15	0.2028 (7)	1.1083 (6)	1.1452 (4)	0.051 (2)
N16	0.2374 (6)	1.2499 (5)	1.1974 (3)	0.051 (1)
C17	0.2990 (6)	1.2479 (6)	1.2808 (3)	0.045 (2)
N18	0.3158 (6)	1.1126 (5)	1.3250 (3)	0.055 (2)
C19	0.3779 (8)	1.1042 (7)	1.4159 (4)	0.062 (2)
C20	0.3435 (8)	1.2537 (8)	1.4617 (4)	0.068 (2)
C21	0.4033 (7)	1.3934 (6)	1.4117 (3)	0.057 (2)
N22	0.3396 (6)	1.3813 (5)	1.3208 (3)	0.057 (2)

Table 2. Selected geometric parameters (Å, °)

O1—C2	1.436 (6)	C11—N12	1.492 (7)
O1—C6	1.374 (6)	N12—C13	1.498 (7)
C2—C3	1.528 (8)	C13—C14	1.519 (8)
C2—C11	1.486 (7)	C14—C15	1.502 (8)
C3—C4	1.505 (8)	C15—N16	1.455 (7)
C4—C5	1.497 (8)	N16—C17	1.322 (6)
C5—C6	1.393 (8)	C17—N18	1.335 (6)
C5—C10	1.389 (8)	C17—N22	1.312 (6)
C6—C7	1.395 (8)	N18—C19	1.434 (7)
C7—C8	1.397 (9)	C19—C20	1.490 (9)
C8—C9	1.36 (1)	C20—C21	1.514 (8)
C9—C10	1.40 (1)	C21—N22	1.438 (7)
C2—O1—C6	116.5 (4)	C5—C10—C9	121.3 (6)
O1—C2—C11	105.5 (4)	C2—C11—N12	111.3 (4)
O1—C2—C3	111.1 (4)	C11—N12—C13	115.6 (4)
C3—C2—C11	112.5 (4)	N12—C13—C14	113.3 (4)
C2—C3—C4	110.6 (5)	C13—C14—C15	114.8 (5)
C3—C4—C5	112.4 (5)	C14—C15—N16	113.9 (4)
C4—C5—C10	122.0 (5)	C15—N16—C17	123.4 (4)
C4—C5—C6	120.6 (5)	N16—C17—N22	119.3 (4)
C6—C5—C10	117.4 (5)	N16—C17—N18	120.9 (4)
O1—C6—C5	122.9 (5)	N18—C17—N22	119.8 (4)
C5—C6—C7	121.9 (5)	C17—N18—C19	123.1 (4)
O1—C6—C7	115.2 (5)	N18—C19—C20	111.3 (5)
C6—C7—C8	118.7 (5)	C19—C20—C21	110.3 (5)
C7—C8—C9	120.4 (6)	C20—C21—N22	110.4 (4)
C8—C9—C10	120.2 (6)	C17—N22—C21	124.1 (4)
O1—C2—C11—N12	-53.2 (5)	N12—C13—C14—C15	64.3 (6)
C2—C11—N12—C13	162.2 (4)	C13—C14—C15—N16	172.5 (4)
C11—N12—C13—C14	54.5 (6)	C14—C15—N16—C17	-77.1 (6)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N12—H12A$\cdots$O1	2.25	2.712 (6)	111
N12—H12A$\cdots$Br1'	2.75	3.508 (4)	142
N12—H12B$\cdots$Br1	2.45	3.332 (4)	167
N16—H16$\cdots$Br1"	2.80	3.497 (4)	139
N18—H18$\cdots$Br2'''	2.44	3.225 (4)	153
N22—H22$\cdots$Br2	2.44	3.192 (4)	146

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

The structure was solved by a combination of Patterson and direct methods on the difference structure. Refinement was performed with full-matrix least-squares on F^2 for all reflections. H atoms were calculated at geometrical positions and allowed to ride on their parent atoms.

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: DIRDIF (Beurskens et al., 1992). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEX2.1b (McArdle, 1994). Software used to prepare material for publication: PARST (Nardelli, 1983).

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Two Photoproducts Derived from 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethoxy-9,10-ethenoanthracene

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Abstract

Photolysis of 11,12-dibenzoyl-9,10-dihydro-9,10-dimethoxy-9,10-ethenoanthracene, (1), in a mixture of benzene and methanol gives the dibenzofuranopentalene (3), whereas irradiation of (1) in a mixture of benzene and aqueous methanol gives a mixture of the dibenzopentalenone (4) and the dibenzofuranopentalene derivative (5). The structures of two of these photoproducts, namely, the methanol solvate of 8c-benzoyl-8b,8c-dihydro-4b,8b-dimethoxy-4bH-dibenzo[a,f]furano-[3,4,5-c,d]pentalene, $C_{32}H_{24}O_4$.0.5CH$_3$OH, (3), and 8c-benzoyl-8b,8c,8d,9-tetrahydro-8b,8d,9-trimethoxy-4bH-dibenzo[a,f]furano[3,4,5-c,d]pentalene, $C_{33}H_{28}O_5$, (5), have been determined by X-ray diffraction methods.

Comment

It has been reported previously that the photolysis of the dibenzobarrelene (1) in benzene, methanol or acetone leads to the dibenzosemibullvalene derivative (2) (Murty, Pratapan, Kumar, Das & George, 1985). In a recent study, it was shown that the photolysis of (1) gives rise to different products depending on the reaction conditions (Kumar, Asokan, Mathew, Ramaiah, Das, Rath & George, 1996). Thus, photolysis of (1) in a mixture of methanol and benzene (4:1) gives a 90% yield of (3) whereas irradiation of (1) in aqueous methanol gives a mixture of (4) (40%) and (5) (34%).
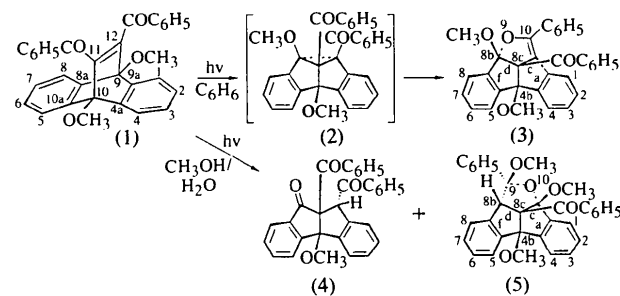
The present study was undertaken in order to confirm the structures of compounds (3) and (5). Compound (3) may arise through the opening of the cyclopropane ring in (2) followed by ring closure analogous to the photo-transformations of 9-aryl-substituted dibenzobarrelenes (Pratapan, Ashok, Gopidas, Rath, Das & George, 1990). Both (4) and (5) may arise through an ionic cleavage of the cyclopropane ring in (2) followed by the loss of a methyl group in the case of (4) and the addition of methanol in the case of (5).

Both (3) and (5) contain a dibenzopentalenofuran skeleton, incorporating a pentacyclic fused-ring core containing two six- and three five-membered rings, which has the shape of a shallow bowl in each case (Figs. 1 and 2). In the case of (3), the methoxy groups at the C4b and C8b positions and the benzoyl group at the C8c position lie on the outer side of the bowl whereas in (5), the benzoyl group at C8c and the methoxy substituent at C4b are *cis* with respect to one another. The 'butterfly angles' formed by the fusion of the two indane systems are 106.5 and 112.3° for compounds (3) and (5), respectively.

Compound (3) crystallizes as a hemisolvate with half a molecule of methanol per molecule. The solvent molecule exhibits large anisotropic thermal motion owing to disorder which could not be resolved. The occupancy factor was refined for the solvent molecule.