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# 4-Phenyl-6,7,8,9-tetrahydro-1*H*-2,3-benzodiazepine 2-Oxide, $C_{15}H_{16}N_2O$

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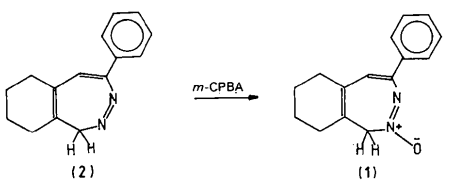
**Abstract.** $M_r = 240{\cdot}3$, monoclinic, $P2_1/c$, $a = 8{\cdot}062$ (2), $b = 13{\cdot}900$ (2), $c = 12{\cdot}007$ (2) Å, $\beta = 108{\cdot}180$ (17)°, $V = 1278{\cdot}4$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}248$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}74$ cm$^{-1}$, $F(000) = 512$, $T = 293$ K. Final $R = 0{\cdot}033$ from 1194 observed reflections. All N—C and C—C single and double bonds are close to expected values, though there is evidence of some delocalization round the seven-membered ring. The N=N and N—O bond lengths are 1·279 (2) and 1·268 (2) Å respectively. The boat conformation adopted by most 1,2-diazepine rings is unperturbed by the oxide ligand which serves to weaken the N=N double bond and lowers the activation energy for ring inversion.

**Introduction.** The title compound (1) was prepared by oxidation of 4-phenyl-6,7,8,9-tetrahydro-1*H*-2,3-benzodiazepine (2) using *m*-chloroperbenzoic acid (*m*-CPBA) (Argo, Robertson & Sharp, 1984). The barrier to ring inversion in the diazepine ring of the oxide (1) is substantially reduced by about 15 kJ mol$^{-1}$ compared with the parent diazepine (2) as determined by variable-temperature $^1$H NMR studies. A crystal-structure analysis was carried out to determine unambiguously the position of oxidation and also to see if there were any structural reasons for the lowering of activation energy for ring inversion.




(2) (1)

**Experimental.** Crystal dimensions 0·3 × 0·25 × 0·25 mm; $D_m$ not measured. Nonius CAD-4 diffractometer, graphite monochromator. 20 reflections used to measure lattice parameters. No correction for absorption. Intensities of 1777 unique reflections measured out to $\theta = 23°$, $h$ −8 to 8, $k$ 0 to 15, $l$ 0 to 13, 1194 reflections with $I > 2{\cdot}5\sigma(I)$ used in refinement. Standard reflections $\bar{2}54$ and $\bar{2}2\bar{2}$ showed no measurable variation. Structure solved by direct methods (*SHELX*76, Sheldrick, 1976) and refined by full-matrix least squares on $F$. All hydrogen atoms located and positional and isotropic thermal parameters refined. Non-hydrogen atoms refined anisotropically. Weighting scheme $w = 1/[\sigma^2(F) + 0{\cdot}00035F^2]$ which gave final $R = 0{\cdot}033$, $wR = 0{\cdot}038$. Maximum ratio of least-squares shift to error in final refinement cycle 0·04. Maximum and minimum peak heights in final difference map 0·1 and −0·22 e Å$^{-3}$. No correction for secondary extinction. Atomic scattering factors from *SHELX*76.

**Discussion.** Table 1 contains positional and mean isotropic thermal parameters for all atoms.* Bond lengths, angles and torsion angles are given in Table 2. A drawing of the molecule is given in Fig. 1. A literature search using the Cambridge Structural Database (1984) revealed 20 crystal structures containing a diazepine seven-membered ring with adjacent nitrogen atoms. Unlike the widely studied 1,4-diazepines (Crippen, 1982), no pharmacological activity has been reported for the 1,2 ring system.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42233 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates of atoms with standard deviations and isotropic thermal parameters*

| | *x* | *y* | *z* | $U_{eq}$*/$U$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 0·1322 (3) | 0·20068 (16) | 1·14596 (24) | 0·0506 |
| N(2) | 0·20414 (22) | 0·27156 (12) | 1·07930 (17) | 0·0455 |
| N(3) | 0·22614 (22) | 0·25045 (11) | 0·98115 (16) | 0·0444 |
| C(4) | 0·1959 (3) | 0·15560 (13) | 0·94008 (19) | 0·0405 |
| C(5) | 0·2449 (3) | 0·07440 (15) | 1·00484 (19) | 0·0425 |
| C(51) | 0·3194 (3) | 0·06841 (14) | 1·13045 (18) | 0·0397 |
| C(6) | 0·4496 (4) | −0·01129 (17) | 1·17882 (20) | 0·0503 |
| C(7) | 0·4953 (4) | −0·02108 (18) | 1·31129 (22) | 0·0619 |
| C(8) | 0·5306 (4) | 0·07696 (19) | 1·36862 (25) | 0·0642 |
| C(9) | 0·3676 (4) | 0·13934 (19) | 1·32979 (22) | 0·0617 |
| C(91) | 0·2757 (3) | 0·13172 (14) | 1·20090 (18) | 0·0429 |
| C(10) | 0·1347 (3) | 0·15191 (14) | 0·80961 (19) | 0·0433 |
| C(11) | 0·1787 (3) | 0·22335 (18) | 0·74296 (22) | 0·0542 |
| C(12) | 0·1232 (4) | 0·21879 (20) | 0·62176 (24) | 0·0657 |
| C(13) | 0·0218 (4) | 0·14315 (20) | 0·5650 (3) | 0·0648 |
| C(14) | −0·0229 (4) | 0·07226 (21) | 0·62978 (24) | 0·0647 |
| C(15) | 0·0323 (3) | 0·07578 (18) | 0·75054 (22) | 0·0557 |
| O(1) | 0·25000 (20) | 0·35298 (9) | 1·12646 (14) | 0·0599 |
| H(11) | 0·028 (3) | 0·1706 (15) | 1·0872 (20) | 0·0550 |
| H(12) | 0·102 (3) | 0·2404 (16) | 1·2025 (19) | 0·0562 |
| H(51) | 0·2454 (23) | 0·0173 (15) | 0·9639 (16) | 0·0423 |
| H(61) | 0·403 (3) | −0·0709 (17) | 1·1434 (19) | 0·0564 |
| H(62) | 0·553 (3) | 0·0018 (16) | 1·1579 (19) | 0·0549 |
| H(71) | 0·596 (3) | −0·0632 (19) | 1·3401 (21) | 0·0734 |
| H(72) | 0·390 (3) | −0·0519 (19) | 1·3347 (22) | 0·0771 |
| H(81) | 0·622 (3) | 0·1073 (20) | 1·3392 (23) | 0·0852 |
| H(82) | 0·572 (3) | 0·0736 (18) | 1·455 (3) | 0·0805 |
| H(91) | 0·285 (3) | 0·1255 (17) | 1·3758 (22) | 0·0693 |
| H(92) | 0·397 (3) | 0·2072 (18) | 1·3456 (19) | 0·0614 |
| H(111) | 0·244 (3) | 0·2748 (17) | 0·7828 (21) | 0·0661 |
| H(121) | 0·157 (3) | 0·2686 (18) | 0·5799 (21) | 0·0710 |
| H(131) | −0·017 (3) | 0·1407 (20) | 0·480 (3) | 0·0925 |
| H(141) | −0·089 (3) | 0·0184 (19) | 0·5925 (22) | 0·0752 |
| H(151) | 0·006 (3) | 0·0268 (18) | 0·7965 (21) | 0·0710 |

* $U_{eq} = \frac{1}{3}$ trace U.

Bond lengths fit reasonably well with the system of localized single and double bonds shown in (1). Values of C(4)–C(5) = 1·358, C(51)–C(91) = 1·341, and N(2)–N(3) = 1·279 Å are only slightly longer than expected double-bond values. The only other 1,2-diazepine X-ray crystal structure with a similar pattern of single and double bonds round the ring is 1-methyl-4-phenyl-1*H*-2,3-benzodiazepine, MPBZZP (Gould & Gould, 1974), which has a significantly shorter N=N double bond of 1·255 (3) Å, and also a shorter N(2)–C(1) bond of 1·477 (3) Å, compared to 1·496 Å in (1). This suggests that the electron-withdrawing oxygen ligand on N(2) acts to delocalize and weaken these bonds. In another related structure diiron hexacarbonyl 5,7-dimethyl-3*H*-1,2-diazepine, BAGRUW (Gould & Walkinshaw, 1981), the electron-withdrawing diiron ligand binds to both nitrogen atoms, and the N–N bond expands to 1·398 Å.

All bond angles are around expected values, though a general feature of 1,2-diazepine rings appears to be the presence of at least one wide angle (in some cases up to 130°) at an $sp^2$ carbon atom. In this structure, intra-ring bond angles at C(5) and C(4) are 126·8 and 126·3° respectively. There is also a tendency for the angle at an $sp^3$ ring carbon to be narrow, though in this compound the intra-ring angle at C(1) is unexceptional at 106·5°.

Torsion angles in Table 2 define the conformation of the molecule. The plane defined by C(51)–C(91)–N(2)–N(3) forms interplanar angles of 120° with the plane C(91)–C(1)–N(2), and 147° with the plane C(51)–C(5)–C(4)–N(3). This describes the ring as a flat-bottomed boat with C(1) at the prow. Nearly

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

| | | | |
|---|---|---|---|
| C(1)–N(2) | 1·496 (3) | C(7)–H(72) | 1·06 (3) |
| C(1)–C(91) | 1·489 (3) | C(8)–C(9) | 1·521 (4) |
| C(1)–H(11) | 1·005 (23) | C(8)–H(81) | 1·00 (3) |
| C(1)–H(12) | 0·963 (23) | C(8)–H(82) | 0·98 (3) |
| N(2)–N(3) | 1·2794 (25) | C(9)–C(91) | 1·497 (4) |
| N(2)–O(1) | 1·2679 (24) | C(9)–H(91) | 1·01 (3) |
| N(3)–C(4) | 1·402 (3) | C(9)–H(92) | 0·977 (24) |
| C(4)–C(5) | 1·358 (3) | C(10)–C(11) | 1·389 (3) |
| C(4)–C(10) | 1·489 (3) | C(10)–C(15) | 1·392 (3) |
| C(5)–C(51) | 1·441 (3) | C(11)–C(12) | 1·384 (4) |
| C(5)–H(51) | 0·933 (20) | C(11)–H(111) | 0·927 (25) |
| C(51)–C(6) | 1·512 (3) | C(12)–C(13) | 1·375 (4) |
| C(51)–C(91) | 1·341 (3) | C(12)–H(121) | 0·94 (3) |
| C(6)–C(7) | 1·523 (4) | C(13)–C(14) | 1·372 (4) |
| C(6)–H(61) | 0·952 (23) | C(13)–H(131) | 0·96 (3) |
| C(6)–H(62) | 0·958 (23) | C(14)–C(15) | 1·378 (4) |
| C(7)–C(8) | 1·513 (4) | C(14)–H(141) | 0·95 (3) |
| C(7)–H(71) | 0·97 (3) | C(15)–H(151) | 0·940 (25) |
| | | | |
| N(2)–C(1)–C(91) | 106·46 (19) | C(7)–C(8)–C(9) | 110·59 (24) |
| C(1)–N(2)–N(3) | 122·02 (18) | C(8)–C(9)–C(91) | 112·21 (22) |
| C(1)–N(2)–O(1) | 117·17 (18) | C(1)–C(91)–C(51) | 117·61 (19) |
| N(3)–N(2)–O(1) | 120·74 (18) | C(1)–C(91)–C(9) | 118·56 (20) |
| N(2)–N(3)–C(4) | 118·74 (18) | C(51)–C(91)–C(9) | 123·78 (20) |
| N(3)–C(4)–C(5) | 126·35 (19) | C(4)–C(10)–C(11) | 121·40 (20) |
| N(3)–C(4)–C(10) | 111·50 (17) | C(4)–C(10)–C(15) | 120·74 (20) |
| C(5)–C(4)–C(10) | 121·04 (19) | C(11)–C(10)–C(15) | 117·86 (21) |
| C(4)–C(5)–C(51) | 126·81 (20) | C(10)–C(11)–C(12) | 121·07 (24) |
| C(5)–C(51)–C(6) | 117·19 (19) | C(11)–C(12)–C(13) | 120·2 (3) |
| C(5)–C(51)–C(91) | 121·09 (19) | C(12)–C(13)–C(14) | 119·3 (3) |
| C(6)–C(51)–C(91) | 121·72 (20) | C(13)–C(14)–C(15) | 121·0 (3) |
| C(51)–C(6)–C(7) | 112·27 (21) | C(10)–C(15)–C(14) | 120·54 (24) |
| C(6)–C(7)–C(8) | 110·15 (23) | | |
| | | | |
| C(91)–C(1)–N(2)–N(3) | 75·63 (25) | C(5)–C(51)–C(91)–C(1) | 7·3 (3) |
| C(91)–C(1)–N(2)–O(1) | −101·44 (21) | C(5)–C(51)–C(91)–C(9) | −170·10 (21) |
| N(2)–C(1)–C(91)–C(51) | −72·30 (25) | C(6)–C(51)–C(91)–C(1) | −173·38 (21) |
| N(2)–C(1)–C(91)–C(9) | 105·27 (23) | C(6)–C(51)–C(91)–C(9) | 9·2 (3) |
| C(1)–N(2)–N(3)–C(4) | −5·6 (3) | C(51)–C(6)–C(7)–C(8) | −45·8 (3) |
| O(1)–N(2)–N(3)–C(4) | 171·40 (18) | C(6)–C(7)–C(8)–C(9) | 63·2 (3) |
| N(2)–N(3)–C(4)–C(5) | −42·2 (3) | C(7)–C(8)–C(9)–C(91) | −43·4 (3) |
| N(2)–N(3)–C(4)–C(10) | 149·78 (19) | C(8)–C(9)–C(91)–C(1) | −169·60 (22) |
| N(3)–C(4)–C(5)–C(51) | 7·7 (4) | C(8)–C(9)–C(91)–C(51) | 7·8 (3) |
| C(10)–C(4)–C(5)–C(51) | 174·67 (20) | C(4)–C(10)–C(11)–C(12) | 179·15 (23) |
| N(3)–C(4)–C(10)–C(11) | 26·9 (3) | C(15)–C(10)–C(11)–C(12) | −0·3 (4) |
| N(3)–C(4)–C(10)–C(15) | −153·68 (21) | C(4)–C(10)–C(15)–C(14) | −179·47 (23) |
| C(5)–C(4)–C(10)–C(11) | −141·80 (24) | C(11)–C(10)–C(15)–C(14) | 0·0 (4) |
| C(5)–C(4)–C(10)–C(15) | 37·6 (3) | C(10)–C(11)–C(12)–C(13) | 0·4 (4) |
| C(4)–C(5)–C(51)–C(6) | −147·15 (23) | C(11)–C(12)–C(13)–C(14) | −0·3 (4) |
| C(4)–C(5)–C(51)–C(91) | 32·2 (3) | C(12)–C(13)–C(14)–C(15) | 0·0 (4) |
| C(5)–C(51)–C(6)–C(7) | −170·18 (21) | C(13)–C(14)–C(15)–C(10) | 0·2 (4) |
| C(91)–C(51)–C(6)–C(7) | 10·5 (3) | | |

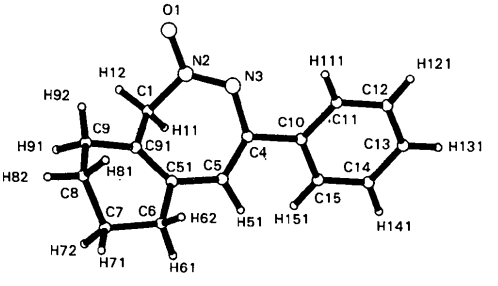


Fig. 1. Labelled drawing of the title compound.

identical interplanar angles are found in MPBZZP, though the diiron complex BAGRUW forms a slightly flatter boat with corresponding angles of 127 and 153°.

Most 1,2-diazepine rings, even with different double-bond positions and widely differing substituents, adopt similar boat conformations. It seems likely, therefore, that the parent 1,2-diazepine (2) would have a similar conformation to the oxide form. The lower barrier to inversion of the oxide compared to that for (2) is likely, therefore, to result mainly from the reduction of the N=N double-bond character. This would facilitate rotation about bonds and provide a lower-energy pathway for ring inversion.

The van der Waals contacts are mostly within the expected ranges. There is, however, a close intermolecular interaction between a methylene hydrogen atom and the azoxy group with distances H(11)···O(1) = 2·45, H(11)···N(2) = 2·71 and H(11)···N(3) = 2·61 Å.

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# Structure of Diethyl (1*S*)-1-[(1*S*)-10-Camphorsulfonylamino]ethylphosphonate,* $C_{16}H_{30}NO_6PS$


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**Abstract.** $M_r = 395{\cdot}4$, monoclinic, $P2_1$, $a = 11{\cdot}040$ (2), $b = 17{\cdot}367$ (4), $c = 12{\cdot}381$ (3) Å, $\beta = 121{\cdot}5$ (5)°, $V = 2024{\cdot}0$ (9) Å$^3$, $Z = 4$, $D_m = 1{\cdot}31$ (1), $D_x = 1{\cdot}30$ Mg m$^{-1}$, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 2{\cdot}38$ mm$^{-1}$, $F(000) = 848$, $T = 292$ K, $R = 0{\cdot}061$ for 3060 reflexions. There are two crystallographically independent molecules in the asymmetric unit. The main chain in both molecules adopts an anticlinal–[+synclinal(g$^+$)]–[+synclinal(g$^+$)] conformation. The O(ethyl)—P—O—C torsion angles are −120 (1), 81 (1)° for (I) and −153 (1), 92 (1)° for (II). The norbornane skeletons are undistorted with C—C—C bridge angles 93·4 (8) and 92·7 (9)°, respectively. The two independent molecules form a dimer through N—H···O(2) hydrogen bonds. The absolute configuration of the molecules was assigned as (*S*,*S*) with reference to the known *S* configuration of the (1*S*)-10-camphorsulfonyl moiety.


**Introduction.** 1-Aminoalkylphosphonic acids are often reported in the literature as mimetics of the naturally occurring amino acids (Hilderbrand, Curley-Joseph, Lubansky & Henderson, 1982). Although much attention has been paid to them because of their biological importance, the literature concerning the synthesis and absolute configuration of these compounds in optically active forms is still scarce (Głowiak, Sawka-Dobrowolska, Kowalik, Mastalerz, Soroka & Zoń, 1977; Vasella & Voeffray, 1982; Kowalik, Sawka-Dobrowolska & Głowiak, 1984).

In our research in this field we encountered some difficulties because of the lack of 1-aminoalkylphosphonic acids in crystalline form suitable for X-ray examination.

In this work we present the crystal structure and absolute configuration of the *N*-(10-camphorsulfonyl) derivative of diethyl 1-aminoethylphosphonate. We believe that this *N*-blocking group will be suitable in our attempts to solve the problem of absolute configuration of other optically active aminophosphonates.

**Experimental.** Title compound obtained by reaction of optically active diethyl 1-aminoethylphosphonate with (1*S*)-10-camphorsulfonyl chloride in the presence of

* 10-Camphorsulfonic acid is 7,7-dimethyl-2-oxobicyclo[2.2.1]-hept-1-ylmethanesulfonic acid.

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