Table 3. *Least-squares planes through the disiloxane moieties and the distances (Å) to the plane of the atoms of the seven-membered ring*

The atoms defining the plane are marked with an asterisk. Estimated standard deviations in the least significant digit are given in parentheses.

	Molecule *A* Plane (i)	Molecule *B* Plane (ii)
O(3′)	0·109 (1)*	−0·007 (1)*
Si(1)	−0·098 (2)*	0·006 (2)*
O(4)	−0·007 (2)*	0·001 (2)*
Si(2)	0·107 (2)*	−0·007 (2)*
O(2′)	−0·112 (1)*	0·007 (1)*
C(2′)	0·721 (5)	0·598 (6)
C(3′)	1·187 (5)	0·993 (5)

The least-squares planes with respect to orthogonal axes X, Y and Z are described by:

(i) $-0{\cdot}9648\ (2)X + 0{\cdot}1935\ (9)Y + 0{\cdot}1784\ (12)Z + 4{\cdot}6283\ (33) = 0$
(ii) $0{\cdot}9208\ (3)X + 0{\cdot}1017\ (11)Y - 0{\cdot}3764\ (9)Z + 3{\cdot}6205\ (34) = 0$.

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2-Methyl-4,5,6,7-tetrahydropyrazolo[3,4-*c*]pyridin-3-ol Monohydrate, a Structural Analogue of THIP (4,5,6,7-Tetrahydroisoxazolo[5,4-*c*]pyridin-3-ol)

BY LOTTE BREHM

Royal Danish School of Pharmacy, Department of Chemistry BC, Universitetsparken 2, DK-2100 Copenhagen, Denmark

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Abstract. $C_7H_{11}N_3O.H_2O$, $M_r = 171{\cdot}21$, monoclinic, $P2_1/c$, $a = 8{\cdot}204\ (4)$, $b = 7{\cdot}352\ (3)$, $c = 15{\cdot}320\ (7)$ Å, $\beta = 118{\cdot}52\ (5)°$, $V = 811{\cdot}9\ (6)$ Å^3, D_m (flotation) = 1·40, $D_c = 1{\cdot}401$ Mg m^{-3}, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares methods. The final R value for 1309 observed reflections is 0·044. The molecule is a zwitterion, and the crystal structure is stabilized by a system of hydrogen bonds.

Introduction. Muscimol [5-(aminomethyl)-3-isoxazolol] is a very active and selective GABA (γ-aminobutyric acid) agonist (Johnston, Curtis, DeGroat & Duggan, 1968; Curtis, Duggan, Felix & Johnston, 1971; Krogsgaard-Larsen, Johnston, Curtis, Game & McCulloch, 1975). Using muscimol as a model compound, a comprehensive series of heterocyclic GABA analogues has been developed (Krogsgaard-Larsen, 1978; Krogsgaard-Larsen, Honoré & Thyssen, 1979; Brehm, Krogsgaard-Larsen & Jacobsen, 1979) and studied with respect to various GABA synaptic processes (Krogsgaard-Larsen, Johnston, Curtis, Game & McCulloch, 1975; Krogsgaard-Larsen & Johnston, 1975, 1978). Some muscimol analogues including THIP are very potent GABA agonists *in vivo* and *in vitro* (Krogsgaard-Larsen, Johnston, Lodge & Curtis, 1977). However, 2-methyl-4,5,6,7-tetrahydropyrazolo[3,4-*c*]pyridin-3-ol (2), which is a structural analogue of THIP in which the 3-isoxazolol moiety has been replaced by a related heterocyclic ring, showed no affinity for the GABA receptors *in vitro* (Krogsgaard-Larsen & Roldskov Christiansen, 1979).

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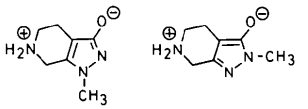

(I) (II)

A separable mixture of two isomeric compounds was obtained after treatment of the appropriate N-protected cyclic β-oxoester with methylhydrazine. The corresponding zwitterions were obtained by acid-catalyzed deprotection and subsequent treatment with triethylamine. Based on spectroscopic studies the zwitterions were assigned the structures (1) and (2), respectively (Krogsgaard-Larsen & Roldskov Christiansen, 1979). The object of this study was to confirm the structure of the title compound.

The crystals used for X-ray examination were obtained as rectangular plates by diffusion of ethanol and acetone into an aqueous solution of the compound.

A single crystal of the size 0·35 × 0·31 × 0·13 mm was used for the determination of the unit-cell parameters and for the collection of intensity data on a Picker FACS-1 diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The general techniques employed are as described by Dahl & Larsen (1979). Intensities were measured for the reflections in the hemisphere ($h \geq 0$) with $2{\cdot}4° \leq 2\theta \leq 55{\cdot}0°$. The symmetry-equivalent reflections were averaged and, of the 1866 unique reflections so obtained, 1309 had net intensities greater than 2·5 $\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation of an intensity as calculated from counting statistics. These were regarded as observed reflections and used in the refinement procedure. No absorption corrections were made [μ(Mo $K\alpha$) = 0·113 mm^{-1}].

The structure was solved by direct methods with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined by the least-squares method minimizing $\sum w(|F_o| - k|F_c|)^2$ (XRAY system, 1972). A difference synthesis calculated after anisotropic refinement on the non-H atoms showed the positions for all H atoms (0·5–0·9 e Å^{-3}). In subsequent full-matrix least-squares calculations, an overall scale factor, atomic coordinates for all atoms and anisotropic thermal parameters for the non-H atoms were refined. The thermal parameters for the H atoms were fixed at isotropic values corresponding to those of the non-H atoms to which they are bonded. The weights used in the final cycles of refinement were given by $w^{-1} = 1 + [(|F_o| - 6{\cdot}0)/8{\cdot}5]^2$. The validity of the weighting scheme was demonstrated by the flat variance of $w\Delta F^2$ *versus* F_o and sin θ. The final R and R_w values are 0·044 and 0·056, respectively. Table 1 lists the final atomic coordinates and thermal parameters.* The X-ray atomic scattering factors used were those of Cromer & Mann (1968) for O, N, and C and of Stewart, Davidson & Simpson (1965) for H.

Table 1. *Final positional and thermal* (Å^2) *parameters*

	x	y	z	B_{eq}*
N(1)	0·4127 (2)	0·6295 (2)	0·1081 (1)	2·03
N(2)	0·3411 (2)	0·6192 (2)	0·1729 (1)	1·76
C(3)	0·1575 (2)	0·6654 (2)	0·1298 (1)	1·52
C(4)	−0·0739 (3)	0·7722 (3)	−0·0530 (1)	1·71
C(5)	−0·0454 (3)	0·8305 (3)	−0·1401 (1)	2·13
N(6)	0·0846 (2)	0·7049 (2)	−0·1546 (1)	2·03
C(7)	0·2781 (3)	0·7149 (3)	−0·0698 (1)	2·23
C(8)	0·2688 (3)	0·6868 (3)	0·0241 (1)	1·78
C(9)	0·1085 (2)	0·7148 (3)	0·0320 (1)	1·66
C(10)	0·4570 (3)	0·5652 (4)	0·2750 (2)	2·39
O(1)	0·0595 (2)	0·6520 (2)	0·1760 (1)	1·99
O(*W*)	0·7153 (3)	0·8212 (3)	0·0980 (2)	4·40
				B_{iso}
H(41)	−0·163 (3)	0·673 (3)	−0·074 (2)	1·7
H(42)	−0·126 (3)	0·880 (3)	−0·036 (2)	1·7
H(51)	−0·162 (3)	0·826 (3)	−0·202 (2)	2·1
H(52)	0·011 (3)	0·952 (3)	−0·127 (2)	2·1
H(61)	0·043 (3)	0·585 (3)	−0·161 (2)	2·1
H(62)	0·092 (3)	0·734 (3)	−0·208 (2)	2·1
H(71)	0·357 (3)	0·623 (3)	−0·079 (2)	2·2
H(72)	0·324 (3)	0·838 (3)	−0·071 (2)	2·2
H(101)	0·386 (3)	0·501 (4)	0·298 (2)	2·4
H(102)	0·555 (3)	0·486 (4)	0·281 (2)	2·4
H(103)	0·520 (3)	0·664 (4)	0·313 (2)	2·4
H(*W*1)	0·645 (5)	0·751 (5)	0·112 (2)	4·4
H(*W*2)	0·821 (5)	0·751 (5)	0·115 (2)	4·4

* $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$. The e.s.d.'s are less than 0·09 Å^2.

Discussion. The X-ray diffraction analysis has shown that the title compound is isomer (2) which, as anticipated from the pK_A values, 5·76 (5) and 9·81 (4) (Krogsgaard-Larsen & Roldskov Christiansen, 1979), crystallizes in the zwitterionic form. The conformation of the molecule found in the crystalline state, numbering of the atoms and ellipsoids of thermal vibrations are shown in Fig. 1. Selected torsion angles are shown in Table 2, and Table 3 shows the deviations of the atoms from the best least-squares plane through the pyrazole ring. The substituents are significantly displaced from the plane, and O(1) and the methyl C(10) are displaced to opposite sides. The six-membered ring adopts a distorted half-chair conformation.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36860 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

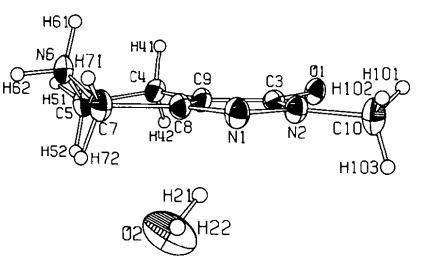

Fig. 1. Perspective drawing (*ORTEP*, Johnson, 1971) of the molecule showing the numbering of the atoms and the thermal ellipsoids for the non-H atoms with a probability of 50%; H atoms are represented as spheres of arbitrary radius.

Table 2. *Molecular dimensions*

Bond lengths (Å)

N(1)–N(2)	1·376 (3)	C(4)–C(5)	1·522 (3)
N(2)–C(3)	1·368 (2)	C(5)–N(6)	1·505 (3)
C(3)–C(9)	1·401 (2)	N(6)–C(7)	1·498 (2)
C(9)–C(8)	1·392 (3)	C(7)–C(8)	1·491 (3)
C(8)–N(1)	1·333 (2)	N(2)–C(10)	1·445 (3)
C(9)–C(4)	1·501 (2)	C(3)–O(1)	1·304 (3)

Valency angles (°)

C(8)–N(1)–N(2)	103·2 (2)	C(4)–C(9)–C(8)	123·9 (2)
N(1)–N(2)–C(3)	112·9 (1)	C(9)–C(8)–N(1)	113·6 (2)
N(1)–N(2)–C(10)	120·6 (2)	N(1)–C(8)–C(7)	123·1 (2)
C(3)–N(2)–C(10)	126·5 (2)	C(7)–C(8)–C(9)	123·3 (1)
N(2)–C(3)–C(9)	105·6 (2)	C(9)–C(4)–C(5)	109·4 (2)
C(9)–C(3)–O(1)	131·6 (1)	C(4)–C(5)–N(6)	111·9 (2)
N(2)–C(3)–O(1)	122·8 (1)	C(5)–N(6)–C(7)	112·0 (1)
C(3)–C(9)–C(8)	104·7 (1)	N(6)–C(7)–C(8)	108·0 (2)
C(3)–C(9)–C(4)	131·2 (2)		

Torsion angles (°)

C(7)–C(8)–C(9)–C(4)	±1·4 (3)	N(6)–C(7)–C(8)–C(9)	∓21·3 (3)
C(8)–C(9)–C(4)–C(5)	∓11·3 (3)	C(10)–N(2)–C(3)–O(1)	∓5·6 (3)
C(9)–C(4)–C(5)–N(6)	±41·8 (2)	C(3)–N(2)–C(10)–H(101)	±33 (2)
C(4)–C(5)–N(6)–C(7)	∓66·5 (2)	N(1)–N(2)–C(10)–H(102)	∓29 (2)
C(5)–N(6)–C(7)–C(8)	±52·3 (2)	N(1)–N(2)–C(10)–H(103)	±85 (2)

Table 3. *Deviations* (Å) *of atoms from the least-squares plane*

Atoms marked with an asterisk were used to calculate the plane; e.s.d.'s are less than 0·01 Å.

N(1)	−0·002*	C(8)	−0·006*	C(5)	0·167
N(2)	0·009*	O(1)	−0·105	N(6)	−0·585
C(3)	−0·012*	C(10)	0·049	C(7)	−0·048
C(9)	0·011*	C(4)	−0·043		

Table 2 lists the bond lengths and angles. There is a pronounced delocalization of π electrons in the 3-pyrazolol anion moiety, *cf.* Table 2, and the molecular dimensions of the pyrazole ring are close to those derived by X-ray diffraction (Berthou, Elguero & Rérat, 1970; La Cour & Rasmussen, 1973), neutron diffraction (Larsen, Lehmann, Søtofte & Rasmussen, 1970) and microwave spectroscopy (Nygaard, Christensen, Nielsen, Pedersen, Snerling, Vestergaard & Sørensen, 1974). The nine C–H bond distances are found to be within the range of 0·92–0·99 Å.

The intramolecular distances from N(6) to N(1), N(2), and O(1) are 3·661 (3), 4·463 (3), and 5·181 (3) Å, respectively. The corresponding distances in the potent GABA agonist THIP, measured on a stereomodel, are of the same magnitudes.

The molecular packing is illustrated in Fig. 2. The crystal structure is apparently stabilized by hydrogen bonds, one for each H atom covalently bonded to N or O. The *c*-glide-plane-related zwitterions are connected by the hydrogen bond N(6)–H(62)···O(1^{iii}), thereby forming infinite chains in the **c** direction. These chains are interlinked by pairs of hydrogen bonds [N(6)–H(61)···O(1^{ii}), O(1)···H(61^{ii})–N(6^{ii})], formed between zwitterions related by a centre of symmetry. The water molecule connects zwitterions related by the translation **a**, the hydrogen bonds being O(W)–H(W1)···N(1^{i}) and O(W)–H(W2)···O(1^{iv}), respectively. Hydrogen-bond distances and angles are given in Table 4. All other *inter*molecular contacts correspond to van der Waals interactions, the shortest contacts being between O(W) and H(72) and H(101), 2·53 (2) and 2·50 (3) Å, respectively.

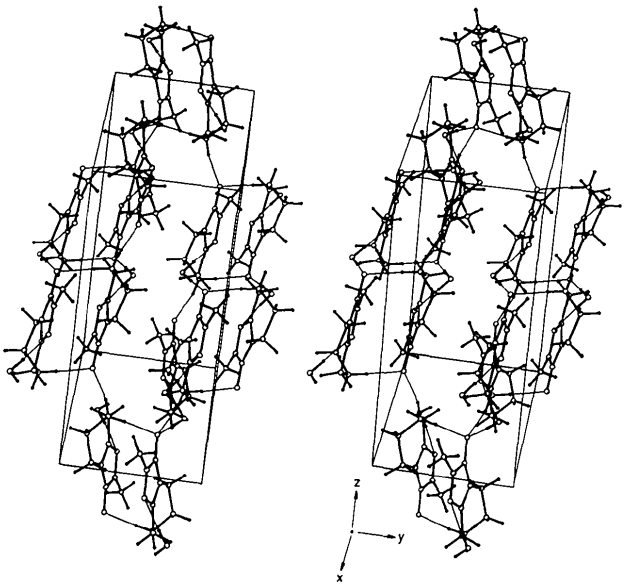

Fig. 2. Stereoscopic view of the molecular packing. Hydrogen bonds are drawn with solid lines.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

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

A–H···*B*	*A*–H	H···*B*	*A*···*B*	∠*AHB*
N(6)–H(61)···O(1^{ii})	0·93 (2)	1·90 (2)	2·832 (2)	176 (2)
N(6)–H(62)···O(1^{iii})	0·88 (3)	1·87 (3)	2·716 (3)	163 (2)
O(W)–H(W1)···N(1^{i})	0·87 (4)	2·08 (4)	2·922 (4)	162 (3)
O(W)–H(W2)···O(1^{iv})	0·93 (4)	1·87 (4)	2·780 (3)	165 (3)

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N-Nitrosodiphenylamine

BY A. BANERJEE, C. J. BROWN AND J. F. P. LEWIS

Department of Metallurgy and Materials Engineering, City of London Polytechnic, Central House, Whitechapel High Street, London E1 7PF, England

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Abstract. $C_{12}H_{10}N_2O$, $M_r = 198{\cdot}08$, monoclinic, $C2/c$, $a = 16{\cdot}283$ (20), $b = 8{\cdot}827$ (10), $c = 16{\cdot}508$ (20) Å, $\beta = 117{\cdot}53$ (15)°, $V = 2104{\cdot}03$ Å^3, $D_m = 1{\cdot}25$, $D_c = 1{\cdot}251$ Mg m^{-3}, $Z = 8$, λ(Cu $K\alpha$) = 1·5418 Å, $F(000) = 832$, $R = 0{\cdot}067$ for 807 observed reflexions. The structure comprises discrete molecules with no intermolecular interactions other than van der Waals forces.

Introduction. *N*-Nitrosodiphenylamine is a brown crystalline solid readily obtainable by reacting diphenylamine with nitrous acid, and is used industrially as an anti-oxidant to slow the curing of rubber. Our sample was supplied by Imperial Chemical Industries Limited (trade name 'Vulcatard A') and the commerical material was purified by recrystallization from absolute ethanol. Unit-cell dimensions were obtained first from layer-line measurements on rotation photographs about several axes, but as the crystals were equi-dimensional with very similar a, c and [101]-axis lengths, their identification was difficult. No reflexions were observable in the high-angle region of Weissenberg photographs so the best values of the lattice parameters were calculated from the 2θ measurements of specific indexed reflexions.

Intensities were obtained from visual estimations of multiple-film Weissenberg photographs of layers $h0l$–$h5l$ and $hk0$ which was also used for inter-layer scaling. The data were corrected for Lp effects but not for absorption, which was small. The structure was determined with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1978) and refined using the NRC suite of programs (Ahmed, Hall, Pippy & Huber, 1973). There were 1067 reflexions within the region examined, of which 260 were $< 1{\cdot}0$ on the scale used.

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