

# 1,4-Bis(2-salicylideneaminoethyl)piperazine, a Sexidentate Binucleating Ligand

BY B. CHIARI, O. PIOVESANA AND T. TARANTELLI

Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 06100 Perugia, Italy

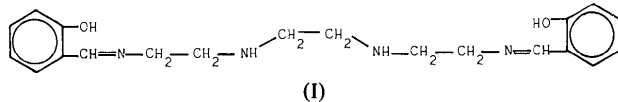
AND P. F. ZANAZZI\*

Cattedra di Cristallografia, Istituto di Mineralogia dell'Università, Piazza Università, 06100 Perugia, Italy

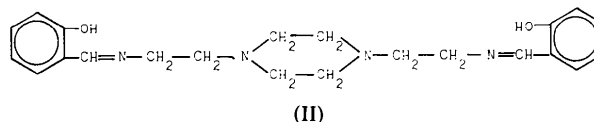
(Received 13 October 1980; accepted 29 June 1981)

**Abstract.**  $C_{22}H_{28}N_4O_2$ ,  $M_r = 380$ , monoclinic,  $P2_1/a$ ,  $a = 13.328$  (3),  $b = 11.654$  (2),  $c = 6.384$  (2) Å,  $\beta = 94.02$  (1)°,  $V = 989.2$  Å<sup>3</sup>,  $D_x = 1.141$  Mg m<sup>-3</sup>,  $Z = 2$ . The structure was solved by direct methods and refined to  $R = 0.048$  for 956 observed reflections. The molecules lie on crystallographic inversion centers; the piperazine ring has the chair conformation. Inter-molecular H bonds (2.589 Å) between O and N are present.

**Introduction.** There is continuing interest in the nature of the spin-spin interactions in magnetically condensed systems (Hodgson, 1975). The main reason for this is the fundamental importance of exchange interactions in theories of chemical bonding and in research in magnetic materials. Bridged dimers formed by Schiff bases and other ligands with paramagnetic metals are of particular interest in this regard because as a group they present a wide variety of structural types and magnetic interactions. Schiff base (I) is known to act as a sexidentate ligand in a variety of metal complexes (Sinn, Sim, Dose, Tweedle & Wilson, 1978) which, apparently because of the considerable flexibility of (I), are all mononuclear.



The steric constraint imposed by the presence of the piperazine ring should coax ligand (II) more than (I) into coordinating to two metal centers. This might afford an opportunity of systematically studying the effect of small variations in molecular structure on exchange coupling by preparing series of related dimeric compounds that differ in a controlled manner. Accordingly, we have synthesized ligand (II). In order to understand the detailed stereochemical and electronic structural changes of the ligand accompanying complex formation, an X-ray structural determination of (II) was deemed useful.



The title compound was prepared by reacting the novel Schiff base 2-bromo-1-salicylideneaminoethane (obtained from 1-amino-2-bromoethane and salicylaldehyde) with piperazine in benzene. Details of the synthesis will appear elsewhere (Chiari, Piovesana, Tarantelli & Zanazzi, 1981). Recrystallization from methanol afforded yellow crystals with m.p. 422–425

Table 1. Positional and thermal parameters with *e.s.d.*'s in parentheses

For non-hydrogen atoms  $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}$ or $U_{eq}$ (Å <sup>2</sup> )
O	0.6236 (2)	0.2642 (2)	0.1386 (4)	0.059 (1)
N(1)	0.6805 (2)	0.3307 (2)	-0.2214 (5)	0.048 (2)
N(2)	0.9255 (2)	0.4295 (2)	-0.4084 (5)	0.038 (2)
C(1)	0.5318 (2)	0.3055 (3)	0.0753 (7)	0.042 (2)
C(2)	0.4548 (2)	0.2956 (3)	0.2110 (7)	0.047 (2)
C(3)	0.3607 (3)	0.3384 (3)	0.1520 (7)	0.050 (2)
C(4)	0.3412 (3)	0.3903 (3)	-0.0422 (3)	0.056 (2)
C(5)	0.4167 (2)	0.3989 (3)	-0.1753 (7)	0.051 (2)
C(6)	0.5128 (2)	0.3566 (2)	-0.1222 (6)	0.039 (2)
C(7)	0.5923 (2)	0.3673 (3)	-0.2668 (7)	0.044 (2)
C(8)	0.7559 (3)	0.3474 (4)	-0.3733 (3)	0.051 (2)
C(9)	0.8437 (2)	0.4131 (3)	-0.2696 (7)	0.045 (2)
C(10)	0.8990 (2)	0.5134 (3)	-0.5726 (7)	0.048 (2)
C(11)	1.0160 (2)	0.4693 (3)	-0.2879 (7)	0.045 (2)
HO	0.668 (4)	0.274 (5)	0.016 (9)	0.12 (2)
H(2)	0.469 (3)	0.257 (4)	0.351 (8)	0.07 (1)
H(3)	0.308 (3)	0.335 (3)	0.235 (7)	0.05 (1)
H(4)	0.277 (3)	0.419 (3)	-0.072 (6)	0.07 (1)
H(5)	0.402 (3)	0.433 (3)	-0.317 (7)	0.06 (1)
H(7)	0.574 (2)	0.405 (3)	-0.399 (6)	0.04 (1)
H(81)	0.784 (3)	0.273 (4)	-0.416 (7)	0.08 (1)
H(82)	0.726 (3)	0.392 (4)	-0.491 (7)	0.06 (1)
H(91)	0.873 (3)	0.364 (4)	-0.158 (7)	0.06 (1)
H(92)	0.820 (2)	0.491 (3)	-0.215 (6)	0.06 (1)
H(101)	0.878 (3)	0.484 (3)	-0.653 (5)	0.06 (1)
H(102)	0.878 (3)	0.590 (3)	-0.510 (6)	0.05 (1)
H(111)	1.002 (3)	0.539 (4)	-0.216 (7)	0.06 (1)
H(112)	1.035 (2)	0.413 (3)	-0.179 (6)	0.04 (1)

\* To whom correspondence should be addressed.

K. A prismatic crystal with dimensions  $0.5 \times 0.2 \times 0.2$  mm was mounted on a PW 1100 four-circle diffractometer equipped with graphite-monochromated Mo radiation. The crystal was monoclinic, space group  $P2_1/a$  (from systematic extinctions). Lattice constants were determined by a least-squares method from the setting angles of 25 reflections. Intensity data were measured with the  $\theta/2\theta$  scan technique in the range  $3 < \theta < 25^\circ$ , with a scan speed of  $0.05^\circ \text{ s}^{-1}$  and a scan width of  $1.6^\circ$ . Lp corrections were applied but no correction for absorption [ $\mu(\text{Mo } K\alpha) = 0.048 \text{ mm}^{-1}$ ] was made; 956 unique reflections with  $I \geq 3\sigma(I)$  were used in the refinement. The structure was solved by direct methods (SHELX 76, Sheldrick, 1976) and refined by full-matrix least squares. H atoms were found in a difference Fourier synthesis and refined with individual isotropic thermal parameters. All nonhydrogen atoms were refined anisotropically.

The refinement converged to  $R = 0.048$ ,  $R_w = 0.055$   $\{R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}\}$  for 183 parameters: reflections were weighted as  $w = 1/[\sigma^2(F_o) + 0.0064F_o^2]$ . Atomic scattering factors of the SHELX system of programs were used. Final atomic coordinates are given in Table 1.\* Bond distances and angles are listed in Tables 2 and 3 respectively.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36198 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å)

O—C(1)	1.350 (4)	O—HO	1.02 (6)
C(1)—C(2)	1.393 (5)	C(2)—H(2)	1.01 (5)
C(2)—C(3)	1.377 (5)	C(3)—H(3)	0.90 (4)
C(3)—C(4)	1.388 (6)	C(4)—H(4)	0.93 (4)
C(4)—C(5)	1.366 (5)	C(5)—H(5)	1.00 (4)
C(6)—C(1)	1.401 (5)	C(7)—H(7)	0.96 (4)
C(6)—C(7)	1.459 (5)	C(8)—H(81)	1.00 (4)
C(7)—N(1)	1.265 (4)	C(8)—H(82)	0.97 (4)
N(1)—C(8)	1.458 (4)	C(9)—H(91)	0.97 (4)
C(8)—C(9)	1.511 (5)	C(9)—H(92)	1.03 (4)
C(9)—N(2)	1.465 (4)	C(10)—H(101)	0.96 (3)
N(2)—C(10)	1.459 (4)	C(10)—H(102)	1.02 (4)
N(2)—C(11)	1.459 (4)	C(11)—H(111)	0.96 (4)
C(10)—C(11)	1.503 (4)	C(11)—H(112)	0.98 (4)
O...N(1)	2.589 (4)		

Symmetry code: (')  $2 - x, 1 - y, -1 - z$ .

Table 3. Bond angles ( $^\circ$ )

O—C(1)—C(2)	118.4 (4)	C(6)—C(7)—N(1)	122.0 (4)
O—C(1)—C(6)	121.5 (3)	C(7)—N(1)—C(8)	118.4 (3)
C(2)—C(1)—C(6)	120.0 (3)	N(1)—C(8)—C(9)	109.0 (3)
C(1)—C(2)—C(3)	119.8 (4)	C(8)—C(9)—N(2)	112.8 (3)
C(2)—C(3)—C(4)	120.8 (4)	C(9)—N(2)—C(10)	111.6 (2)
C(3)—C(4)—C(5)	119.3 (3)	C(9)—N(2)—C(11)	110.2 (3)
C(4)—C(5)—C(6)	121.8 (4)	C(10)—N(2)—C(11)	108.4 (2)
C(5)—C(6)—C(1)	118.3 (3)	N(2)—C(10)—C(11)	111.1 (3)
C(5)—C(6)—C(7)	120.8 (4)	N(2)—C(11)—C(10)	111.1 (3)
C(1)—C(6)—C(7)	120.9 (3)		

**Discussion.** A perspective view of a molecule of the title compound is shown in Fig. 1. The molecule lies on the inversion center. All distances and angles are close to the expected values. The mean C—C distance between  $sp^3$ -hybridized C atoms is 1.507 Å; the C—N double bond is 1.265 Å; the C—N single-bond length averages 1.460 Å; the C—O distance is 1.350 Å; the mean C—H bond length is 0.98 Å. The phenyl ring is planar in the limits of experimental error. The equation of the best ring plane, together with the atomic deviations from it, are reported in Table 4. The average distance between C atoms in the ring is 1.386 Å. The piperazine ring has the chair conformation; the atoms are alternately displaced from the least-squares plane by 0.237 Å. Some torsion angles in the molecule are listed in Table 5.

The molecules are packed in the crystal nearly perpendicularly to the  $z$  axis, and are well separated: no intermolecular contacts shorter than the respective van der Waals diameters were found.

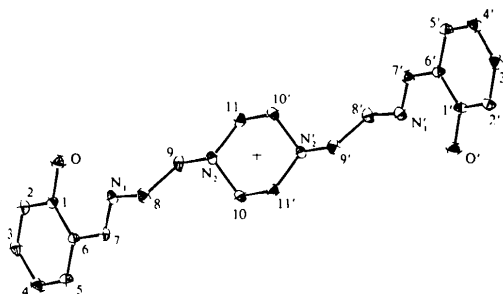


Fig. 1. ORTEP (Johnson, 1965) view of the title compound with the numbering of the atoms.

Table 4. Least-squares planes of the benzene and piperazine rings, and deviations (Å) of atoms from them

The equations of the least-squares planes are given in the form  $Ax + By + Cz = D$  in direct space.

(a) Benzene:  $A = 3.123, B = 10.329, C = 2.439, D = 4.993$

C(1)	0.007	C(4)	0.001	*O	0.023
C(2)	-0.004	C(5)	0.002	*C(7)	0.001
C(3)	0.000	C(6)	-0.006	*N(1)	0.009

(b) Piperazine:  $A = -3.012, B = 10.206, C = 2.818, D = 0.682$

N(2)	-0.237
C(10)	0.237
C(11)	0.237

\* Atoms not included in the calculation of the plane.

Table 5. Torsion angles ( $^\circ$ )

Signs are given according to the convention of Klyne & Prelog (1960). E.s.d.'s are  $0.9^\circ$ .

C(7)—N(1)—C(8)—C(9)	123.0	N(2)—C(11)—C(10)'—N(2)'	59.3
N(1)—C(8)—C(9)—N(2)	177.4	C(11)'—C(10)'—N(2)'—C(11)'	-57.7
C(8)—C(9)—N(2)—C(10)	72.4	C(10)'—N(2)'—C(11)'—C(10)	57.7
C(8)—C(9)—N(2)—C(11)	-167.1		

Tests of the mode of coordination of (II) to bi- or trivalent metal ions ( $\text{Cu}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ) indicate sexidentate binucleating behavior, with a change from a chair to a boat conformation for the piperazine ring. Structural work on these compounds is in progress.

#### References

- CHIARI, B., PIOVESANA, O., TARANTELLI, T. & ZANAZZI, P. F. (1981). *Inorg. Chem.* In the press.
- HODGSON, D. J. (1975). *Prog. Inorg. Chem.* **19**, 173–241.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SINN, E., SIM, G., DOSE, E. V. TWEEDLE, M. F. & WILSON, L. J. (1978). *J. Am. Chem. Soc.* **100**, 3375–3390.

*Acta Cryst.* (1982). **B38**, 333–335

## The Absolute Configuration of the Tropane Alkaloid 6 $\beta$ ,7 $\beta$ -Epoxy-1 $\alpha$ H,5 $\alpha$ H-tropan-3 $\alpha$ -yl (–)-2,3-Dihydroxy-2-phenylpropionate from its *n*-Butylbromide

BY J. BODE AND C. H. STAM\*

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

(Received 27 April 1981; accepted 30 June 1981)

**Abstract.**  $\text{C}_{17}\text{H}_{21}\text{NO}_5 \cdot \text{C}_4\text{H}_9\text{Br}$ ,  $M_r = 456.38$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.215$  (1),  $b = 12.974$  (2),  $c = 22.466$  (2) Å,  $Z = 4$ ,  $D_c = 1.44$  Mg m $^{-3}$ . Final  $R = 0.027$  for 1978 observed reflexions. The tropane alkaloid is narrowly related to scopolamine with an additional OH group at the asymmetric atom of the tropic acid residue. The absolute configuration around this atom is *S*, which is the inverse of that around the corresponding atom in scopolamine.

**Introduction.** Moorhoff (1975) has separated a new alkaloid from extracts of leaves of *Datura sanguinea*, which he identified as 6 $\beta$ ,7 $\beta$ -epoxy-1 $\alpha$ H,5 $\alpha$ H-tropan-3 $\alpha$ -yl (–)-2,3-dihydroxy-2-phenylpropionate. It is narrowly related to scopolamine; instead of tropic acid (3-hydroxy-2-phenylpropionic acid) the new alkaloid contains 2,3-dihydroxy-2-phenylpropionic acid, which has an additional OH group at the asymmetric C atom. The main object of the present structure determination of the *n*-butylbromide of the new alkaloid was to establish the absolute configuration at the asymmetric centre of the 2,3-dihydroxy-2-phenylpropionic acid residue.

1978 reflexions with  $2\theta \leq 130^\circ$  and intensities above the  $2\sigma$  level were measured on a Nonius CAD-4 single-crystal diffractometer employing graphite-monochromatized Cu  $K\alpha$  radiation. No absorption correction was applied (crystal dimensions  $0.3 \times 0.3 \times 0.4$

Table 1. Fractional coordinates ( $\times 10^5$  for Br,  $\times 10^4$  for C,N,O) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Br	5509 (6)	15143 (3)	19336 (2)	39.3 (1)
C(1)	5576 (4)	4611 (3)	3030 (2)	27 (1)
C(2)	5945 (5)	4778 (3)	2362 (2)	35 (1)
C(3)	5542 (5)	3824 (3)	1976 (2)	33 (1)
C(4)	5751 (5)	2763 (3)	2276 (2)	31 (1)
C(5)	5432 (5)	2796 (3)	2952 (2)	27 (1)
C(6)	3462 (5)	3183 (3)	3035 (2)	30 (1)
C(7)	3548 (5)	4300 (3)	3088 (2)	34 (1)
N(8)	6639 (4)	3645 (2)	3226 (2)	21 (1)
O(9)	3045 (4)	3680 (2)	3599 (2)	41 (1)
O(10)	3610 (4)	3860 (2)	1765 (2)	30 (1)
C(11)	3242 (5)	4543 (3)	1333 (2)	33 (1)
O(12)	4391 (5)	5107 (3)	1117 (2)	59 (1)
C(13)	1180 (5)	4556 (3)	1167 (2)	28 (1)
C(14)	545 (6)	5676 (3)	1203 (2)	41 (1)
O(15)	1173 (6)	6165 (3)	1731 (2)	57 (1)
O(16)	99 (4)	4009 (2)	1591 (2)	30 (1)
C(17)	922 (5)	4139 (3)	531 (2)	29 (1)
C(18)	2025 (7)	4494 (3)	71 (2)	46 (1)
C(19)	1769 (8)	4125 (4)	–511 (2)	57 (1)
C(20)	394 (9)	3407 (4)	–620 (2)	65 (2)
C(21)	–723 (11)	3084 (4)	–166 (2)	75 (2)
C(22)	–459 (7)	3434 (4)	413 (2)	50 (1)
C(23)	8615 (5)	3637 (3)	2998 (2)	30 (1)
C(24)	6796 (5)	3505 (3)	3910 (2)	33 (1)
C(25)	7982 (7)	4307 (4)	4219 (2)	49 (1)
C(26)	7887 (7)	4150 (4)	4899 (2)	53 (1)
C(27)	8786 (10)	3206 (5)	5135 (3)	81 (2)

\* To whom correspondence should be addressed.