

These ring conformations are consistent with the *trans-syn-trans-anti-trans* ring junctions (Boeyens, Bull & Van Rooyen, 1980). For related Westphalen compounds chemical-reactivity studies were interpreted in terms of a half-chair conformation for ring *B* whilst NMR studies have shown this ring to be relatively flexible (Glötter *et al.*, 1975).

The  $17\beta$ -side chain exists in the extended conformation which is the most common conformation in cholestane derivatives (Duax, Griffin, Rohrer & Weeks, 1980). All intermolecular contacts between non-H atoms are  $>3.2 \text{ \AA}$ .

We wish to acknowledge grants from the Research Committee of the New Zealand Universities Grants Committee.

#### References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.

BOEYENS, J. C. A., BULL, J. R. & VAN ROOYEN, P. H. (1980). *S. Afr. J. Chem.* **33**, 45–50.

BUCOURT, R. (1974). *Topics in Stereochemistry*, Vol. 8, edited by E. L. ELIEL & N. L. ALLINGER, pp. 159–224. New York: Wiley-Interscience.

COXON, J. M., HOSKINS, P. R. & RIDLEY, T. K. (1977). *Aust. J. Chem.* **30**, 1735–1742.

DUAX, W. L., GRIFFIN, J. F., ROHRER, D. C. & WEEKS, C. M. (1980). *Lipids*, **15**, 783–792.

DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by N. L. ALLINGER & E. L. ELIEL, pp. 271–383. New York: Wiley-Interscience.

GLOTTER, E., RABINSOHN, Y. & OZARI, Y. (1975). *J. Chem. Soc. Perkin Trans. 1*, pp. 2104–2108.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

SHAFIULLAH, GHAFFARI, M. A. & ALI, H. (1980). *Tetrahedron*, **36**, 2263–2265.

SHELDRIK, G. M. (1983). *SHELXTL User Manual*, revision 4. Nicolet XRD Corporation, Cupertino, California.

WESTPHALEN, T. (1915). *Chem. Ber.* **48**, 1064–1069.

*Acta Cryst.* (1985). **C41**, 741–743

## Structure of 1,4-Dinitrosopiperazine, $\text{C}_4\text{H}_8\text{N}_4\text{O}_2$

BY KIYOTANE SEKIDO, KOJUN OKAMOTO\* AND SAKUTARO HIROKAWA

*Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka City, 239 Japan*

(Received 19 September 1984; accepted 14 December 1984)

**Abstract.**  $M_r = 144.13$ , orthorhombic, *Pbca*,  $a = 9.495(4)$ ,  $b = 6.570(3)$ ,  $c = 10.521(7) \text{ \AA}$ ,  $V = 656.3(9) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.459$ ,  $D_m = 1.427 \text{ Mg m}^{-3}$ ,  $\lambda = 0.7107 \text{ \AA}$ ,  $\mu = 0.0877 \text{ mm}^{-1}$ ,  $F(000) = 304$ ,  $T = 293 \text{ K}$ , final  $R = 0.089$  for 959 independent reflections. The molecule is centrosymmetric, the piperazine ring having a chair form. The two nitroso groups are in the *anti* form. The N–O bond length is  $1.202(4) \text{ \AA}$ , and the N–N–O angle  $113.4(3)^\circ$ . The molecules are packed together to form infinite ribbons along the [110] direction.

**Introduction.** As the piperazine system offers a rich selection of conformational questions, molecular shapes of this system have been investigated by NMR, dipole moment, and electron diffraction. Since piperazine derivatives are of interest due to their pharmacological activity and natural occurrence, we have studied the crystal structures of these derivatives by the X-ray method under a current program of this laboratory (Okamoto, Sekido, Itoh, Noguchi & Hirokawa, 1979;

Okamoto, Sekido, Ono, Noguchi & Hirokawa, 1982). 1,4-Dinitrosopiperazine (DNP) was chosen because it possesses several modes of conformational flexibility and it is a potent carcinogen in various animals. Lambert, Gosnell, Bailey & Henkin (1969) reported that the centrosymmetric *anti* form of DNP appeared to be present exclusively in the solid state, but a clear choice between a chair form and a boat form was not provided. The present work was undertaken to obtain the unambiguous structure of DNP.

**Experimental.** Colorless rectangular prismatic crystals (m.p. 430 K) obtained by slow evaporation from an ethanol solution.  $D_m$  measured by flotation in a mixture of toluene and tetrachloromethane. Crystal  $0.5 \times 0.5 \times 0.6 \text{ mm}$ . Rigaku AFC-III four-circle diffractometer,  $\text{Mo K}\alpha$  radiation monochromatized by a graphite plate. X-ray intensity data measured by  $\omega$ - $2\theta$  scan, scan speed  $4^\circ \text{ min}^{-1}$  in  $2\theta$ . Cell dimensions determined by least-squares method *RSLC-3* (UNICS, 1967) using 13 reflections with  $25.0^\circ < \theta < 29.9^\circ$ . Systematic absences  $h = 2n + 1$  in  $hk0$ ,  $k = 2n + 1$  in  $0kl$ , and  $l = 2n + 1$  in  $h0l$ . 959 independent reflections

\* To whom correspondence should be addressed.

measured;  $0 \leq h \leq 13$ ,  $0 \leq k \leq 9$ ,  $0 \leq l \leq 14$ ; standard reflections 400, 020, 006, intensity variation 3.0%;  $(\sin \theta_{\max})/\lambda = 0.7030 \text{ \AA}^{-1}$ ,  $2\theta_{\max} = 59.99^\circ$ ; 644 unique reflections,  $R_{\text{int}} = 0.067$ ; 315 unobserved reflections with  $I < 3\sigma(I)$ . Data corrected for Lorentz and polarization factors but not for absorption. Structure solved by a three-dimensional Patterson synthesis, and refined by block-diagonal least squares using *HBLS-5* (Ashida, 1973) and *RSSFR-5* (*UNICS*, 1967). H-atom positions located on a difference Fourier map. Final cycles of refinement with anisotropic temperature factors for C, N, and O, and isotropic for H atoms.  $R = 0.089$ ,  $wR = 0.090$ ,  $S = 1.62$ .  $\sum w(|F_o| - k|F_c|)^2$  minimized; weighting scheme  $w = 1.0/[\sigma(F_o)]^2$  for  $F_o \neq 0$  and  $w = 1.0$  for  $F_o = 0$ . In final refinement cycle  $(\Delta/\sigma)_{\max} = 0.09$  and max. peak height in final difference map  $0.3 \text{ e \AA}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on a HITAC M-200 (H) computer in the National Defense Academy.

**Discussion.** The numbering scheme and the thermal ellipsoids of the non-hydrogen atoms are illustrated in Fig. 1. The atomic parameters with their standard deviations are shown in Table 1.\* The bond distances and angles are listed in Table 2. Since the molecule is centrosymmetric, the piperazine ring has a chair form (Armarego, 1977), and the nitroso groups are in the *anti* form. The N—C bond length in the piperazine ring, 1.450 (5) Å (mean), is in good agreement with 1.463 Å in 2,5-dimethylpiperazine (DP) (Okamoto, Sekido, Ono, Noguchi & Hirokawa, 1982), 1.459 Å in *trans*-1,4-dibenzoyl-2,5-dimethylpiperazine (*trans*-DDP) (Okamoto, Sekido, Itoh, Noguchi & Hirokawa, 1979), 1.467 Å in piperazine (PZ) (Yokozeki & Kuchitsu, 1971), 1.464 Å in *cis*-1,4-dibenzoyl-2,5-dimethylpiperazine (*cis*-DDP) (Sakurai, Nakamaru, Tsuboyama

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters for non-H atoms

The estimated standard deviations given in parentheses refer to the last decimal position.  $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$ .

	x	y	z	$B_{\text{eq}}$ (Å <sup>2</sup> )
N(1)†	1195 (3)	612 (3)	629 (3)	4.5
C(2)	-140 (4)	710 (4)	1292 (3)	5.2
C(3)	-1148 (3)	-847 (4)	743 (3)	5.1
N(7)	2337 (3)	422 (3)	1361 (3)	5.8
O(8)	3422 (3)	422 (3)	772 (3)	7.3

† N(1), C(2), C(3), N(7), and O(8) are related by a center of symmetry to N(4), C(5), C(6), N(9), and O(10), respectively.

Table 2. Intramolecular distances (Å) and angles (°) between non-H atoms with e.s.d.'s in parentheses

N(1)—C(2)	1.448 (5)	C(2)—C(3)	1.515 (5)
N(1)—C(6)	1.451 (5)	N(7)—O(8)	1.202 (4)
N(1)—N(7)	1.336 (4)		
N(1)...C(3)	2.425 (5)	C(2)...N(7)	2.361 (5)
N(1)...N(4)	2.746 (4)	C(3)...C(5)	2.467 (5)
N(1)...C(5)	2.416 (5)	C(6)...N(7)	2.500 (5)
N(1)...O(8)	2.124 (4)	C(6)...O(8)	2.697 (5)
N(1)—C(2)—C(3)	109.8 (3)	C(2)—N(1)—N(7)	115.9 (3)
C(2)—C(3)—N(4)	109.1 (3)	C(6)—N(1)—N(7)	127.4 (3)
C(2)—N(1)—C(6)	116.6 (3)	N(1)—N(7)—O(8)	113.4 (3)

& Tsuboyama, 1977), and 1.463 Å in 1,4-bis(1,2-dimethyl-1-propenyl)piperazine (Van Meerssche, Germain, Declercq & Colens, 1979). The bond distance of 1.515 (5) Å for C—C is shorter than the  $C(sp^3)$ — $C(sp^3)$  covalent bond length. But this is comparable to 1.521 Å in DP, 1.517 Å in *trans*-DDP, 1.535 Å in *cis*-DDP, and 1.521 Å in *N,N'*-dimethylpiperazine (Davis & Hassel, 1963). The N...N distance of 2.746 (4) Å is slightly shorter than 2.806 Å in *trans*-DDP, and 2.820 Å in *trans*-DP. The bond angles of  $C(sp^3)$  atoms in the piperazine ring are approximately tetrahedral and close to the angles of PZ. The value of 116.6 (3)° for C(2)—N(1)—C(6) agrees with 115.7° in *cis*-DDP, and is larger than 113.8° in *trans*-DDP, and 112.6° in piperidine (Blackburne, Duke, Jones, Kartitzky & Record, 1973).

The ring torsion angles are -51.1 (4), 55.0 (4), and -55.4 (4)° for N(1)—C(2)—C(3)—N(4), C(2)—C(3)—N(4)—C(5), and C(3)—N(4)—C(5)—C(6), respectively. The C(2), C(6), N(1), N(7), and O(8) atoms are coplanar within 0.023 Å. The dihedral angle between the mean plane (1) formed by C(2), C(3), C(5) and C(6) and the mean plane (2) composed of N(1), C(2), C(6), N(7), and O(8) is 48.4 (2)°, which is comparable to those found in *trans*-DP (about 55°) and *trans*-DDP (about 53°).

The value of 113.4 (3)° for N(1)—N(7)—O(8) agrees with 113.6° for N—N—O in dimethylnitrosamine (MNA) (Rademacher & Stolevik, 1969). The N—O bond distance of 1.202 (4) Å is comparable to that

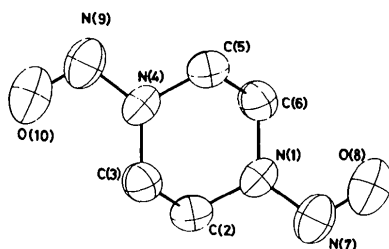


Fig. 1. Numbering scheme and the thermal ellipsoids of the non-hydrogen atoms drawn by ORTEP (Johnson, 1965). The thermal-vibration ellipsoids are set to 50% probability.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39978 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

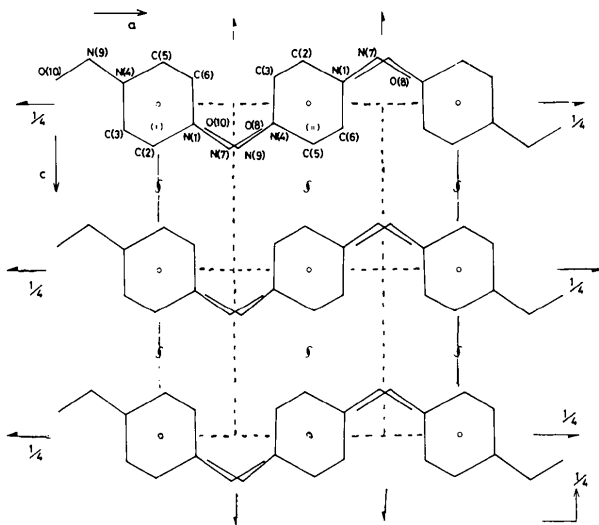


Fig. 2. The molecular packing in the unit cell viewed down the  $b$  axis. Symmetry codes: (i)  $x, y, z$ ; (ii)  $0.5 + x, 0.5 - y, -z$ .

found in MNA ( $1.234 \text{ \AA}$ ). The N—N bond length of  $1.336(4) \text{ \AA}$  is in good agreement with that of  $1.344 \text{ \AA}$  in MNA, and is significantly shorter than the N—N single bond (Liminga & Olovsson, 1964). This shows the N—N double-bond character. Thus the  $C_2NNO$  group results in hindered rotation about the N—N bond (Cooney, Brownstein & ApSimon, 1974).

The molecular packing viewed down the  $b$  axis is shown in Fig. 2. The closest non-bonded approach of  $3.185(4) \text{ \AA}$  is between N(1<sup>i</sup>) and O(10<sup>ii</sup>). The second-shortest contact of  $3.300(6) \text{ \AA}$  is between N(7<sup>i</sup>) and N(9<sup>ii</sup>). The triangular plane formed by N(1<sup>i</sup>), N(7<sup>i</sup>), and O(8<sup>i</sup>) is approximately parallel to the neighboring triangular plane formed by N(4<sup>ii</sup>), N(9<sup>ii</sup>), and O(10<sup>ii</sup>), the dihedral angle being  $10.2(1)^\circ$ . No other short contacts can be seen in the structure. The molecules are packed together to form infinite ribbons along the  $[110]$

direction, and the ribbons are held together in the crystal by van der Waals forces.

The authors would like to thank Mr Yoshiaki Totsuka of Nippon Nyukazai Co. Ltd, Tokyo, for the supply of crystals. They are also indebted to Mr Kazumasa Maruyama and Mr Eiichi Yamamoto for their kind help in the computation.

#### References

- ARMAREGO, W. L. F. (1977). *Stereochemistry of Heterocyclic Compounds*, 1st ed., pp. 189–190. New York: Wiley-Interscience.
- ASHIDA, T. (1973). *HBL5-5. The Universal Crystallographic Computing System—Osaka*, pp. 55–61. The Computation Center, Osaka Univ., Japan.
- BLACKBURN, I. D., DUKE, R. P., JONES, R. A. Y., KATRITZKY, A. R. & RECORD, K. A. F. (1973). *J. Chem. Soc. Perkin Trans. 2*, pp. 332–336.
- COONEY, J. D., BROWNSTEIN, S. K. & APSIMON, J. W. (1974). *Can. J. Chem.* **52**, 3028–3036.
- DAVIS, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**(4), 1181.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LAMBERT, J. B., GOSNELL, J. L., BAILEY, D. S. & HENKIN, B. M. (1969). *J. Org. Chem.* **34**, 4147–4150.
- LIMINGA, R. & OLOVSSON, I. (1964). *Acta Cryst.* **17**, 1523–1528.
- OKAMOTO, K., SEKIDO, K., ITOH, J., NOGUCHI, T. & HIROKAWA, S. (1979). *Bull. Chem. Soc. Jpn.* **52**, 1896–1898.
- OKAMOTO, K., SEKIDO, K., ONO, H., NOGUCHI, T. & HIROKAWA, S. (1982). *Bull. Chem. Soc. Jpn.* **55**, 945–946.
- RADEMACHER, P. & STOLEVIK, R. (1969). *Acta Chem. Scand.* **23**, 660–671.
- SAKURAI, T., NAKAMARU, M., TSUBOYAMA, S. & TSUBOYAMA, K. (1977). *Acta Cryst.* **B33**, 3568–3571.
- UNICS (1967). Editor T. SAKURAI. Programs *RSLC-3* and *RSSF-5*. Tokyo: The Crystallographic Society of Japan.
- VAN MEERSCHKE, M., GERMAIN, G., DECLERCQ, J.-P. & COLENS, A. (1979). *Acta Cryst.* **B35**, 907–913.
- YOKOZEKI, A. & KUCHITSU, K. (1971). *Bull. Chem. Soc. Jpn.* **44**, 2352–2355.

*Acta Cryst.* (1985). **C41**, 743–746

## Structure of 2-[(Hydroxyimino)(phenylthio)methyl]-1-methylpyridinium Chloride, $C_{13}H_{13}N_2OS^+.Cl^-$

BY BARBARA J. OLEKSYN AND KATARZYNA M. STADNICKA

*Faculty of Chemistry, Jagiellonian University, Karasia 3, 30-060 Kraków, Poland*

(Received 27 January 1984; accepted 17 December 1984)

**Abstract.**  $M_r = 280.78$ ,  $P2_1/c$ ,  $a = 9.30(1)$ ,  $b = 11.433(7)$ ,  $c = 14.02(2) \text{ \AA}$ ,  $\beta = 114.8(1)^\circ$ ,  $V = 1353(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.378 \text{ Mg m}^{-3}$ ,  $Mo K\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 0.373 \text{ mm}^{-1}$ ,  $F(000) = 584$ , room

temperature,  $R = 0.037$ , 2513 unique reflections. The oxime moiety of the molecule is in the (*E*) configuration. The molecule has a folded conformation, which may be responsible for its inability to reactivate