

N—C—C—C—N planes in each molecule form interplanar angles of 95.7 (5) and 100.7 (5)°. The average values for C(sp<sup>3</sup>)—C(sp) and C≡N of 1.475 (5) and 1.136 (4) Å in (1) and 1.473 (6) and 1.139 (3) Å in (2) are consistent with values from similar systems (Watson, Kashyap, Bartlett & Wu, 1984; Kashyap, Watson, Wu & Bartlett, 1984; Wang & Stucky, 1973; Karle, Flippen, Huisgen & Schug, 1975). The C(1)—C(2) bond lengths of 1.606 (3) and 1.601 (3) Å, the C(2)—C(3) lengths of 1.612 (2) and 1.620 (2) Å, and the C(3)—C(4) lengths of 1.577 (3) and 1.578 (3) Å in (1) and (2) are consistent with the lengthened bonds observed in the above references. The C(1)—C(2) and C(3)—C(4) lengths are not identical due to differences in interactions of the cyano groups.

The molecules can be considered to be composed of fused five-membered rings in envelope conformations or fused six-membered rings held in boat conformations by methylene bridges. The sixteen valence angles of less than 105° imply considerable ring strain within the molecules. There are no intermolecular contacts in compound (2) less than 2.60 Å but there are three in (1). The shortest contact of 2.37 Å is between H(4) of one molecule and H(8a) of another. Contacts between H(7')...H(8b) and H(4')...H(11c) are about 2.50 Å.

We thank The Robert A. Welch Foundation (P-074) for their financial support. This is FASTBIOS contribution No. 121.

*Acta Cryst.* (1984). **C40**, 869–871

## Structure of 1,2-Dipiperidinoethane Mono-*N*-oxide Monoperchlorate Monohydrate,\* (C<sub>12</sub>H<sub>25</sub>N<sub>2</sub>O)<sup>+</sup>.ClO<sub>4</sub><sup>-</sup>.H<sub>2</sub>O

BY MARIUSZ JASKÓLSKI AND ZOFIA KOSTURKIEWICZ

*Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland*

(Received 16 November 1983; accepted 3 January 1984)

**Abstract.**  $M_r = 330.8$ , monoclinic,  $P2_1/n$ ,  $a = 11.366$  (2),  $b = 6.540$  (1),  $c = 22.082$  (3) Å,  $\beta = 95.52$  (1)°,  $V = 1633.8$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.34$  Mg m<sup>-3</sup>, Cu  $K\alpha$ ,  $\lambda = 1.54178$  Å,  $\mu = 2.34$  mm<sup>-1</sup>,  $F(000) = 712$ , room temperature,  $R = 0.062$  for 1892 observed reflexions. The organic cation is *cisoidal* with a very short intramolecular O...H...N hydrogen bond [O...N 2.551 (4) Å]. The H atom in this heteroatomic bridge appears to be more or less central. Water

\* *N*-(2-Piperidinoethyl)piperidinium *N'*-oxide perchlorate monohydrate.

- ### References
- BARTLETT, P. D. & WU, C. (1983). *J. Am. Chem. Soc.* **105**, 100–104.  
 BARTLETT, P. D. & WU, C. (1984). In preparation.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 KARLE, I., FLIPPEN, J., HUISGEN, R. & SCHUG, R. (1975). *J. Am. Chem. Soc.* **97**, 5285–5287.  
 KASHYAP, R. P., WATSON, W. H., WU, C. & BARTLETT, P. D. (1984). *Acta Cryst.* **C40**, 861–863.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78*. A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.  
 PAQUETTE, L. A., WILLIAMS, R. V., CARR, R. V. C., CHARUMILIND, P. & BLOUNT, J. F. (1982). *J. Org. Chem.* **47**, 4566–4572.  
 PINKERTON, A. A., SCHWARZENBACH, D., STIBBARD, J. H. A., CARRUPT, P.-A. & VOGEL, P. (1981). *J. Am. Chem. Soc.* **103**, 2095–2096.  
 STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 SUBRAMANYAN, R., BARTLETT, P. D., IGLESIAS, G. Y. M., WATSON, W. H. & GALLOY, J. (1982). *J. Org. Chem.* **47**, 4491–4498.  
 WANG, Y. & STUCKY, G. D. (1973). *Acta Cryst.* **B29**, 1255–1258.  
 WATSON, W. H., GALLOY, J., BARTLETT, P. D. & ROOF, A. A. M. (1981). *J. Am. Chem. Soc.* **103**, 2022–2031.  
 WATSON, W. H., KASHYAP, R. P., BARTLETT, P. D. & WU, C. (1984). *Acta Cryst.* **C40**, 863–866.

molecules and the cations are H bonded to form infinite chains in which the H<sub>2</sub>O molecules are double donors and the N—O groups double acceptors.

**Introduction.** Our earlier investigations of the 1,1'-ethylenebis(piperidine 1-oxide) [PEtP(NO)<sub>2</sub>] system revealed that it prefers the *transoidal* conformation (Jaskólski, Kosturkiewicz, Mickiewicz-Wichlacz & Wiewiórowski, 1979; Jaskólski, 1982) unless it is monoprotonated in which case the *cisoidal* form is adopted with the two N—O functions linked by a very short† O...H...O hydrogen bridge (Jaskólski, Gdaniec

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{eq}$
O(1)	0.2344 (3)	-0.0038 (5)	0.6687 (1)	0.053 (1)
N(1)	0.1744 (3)	0.0968 (5)	0.6168 (1)	0.036 (1)
C(12)	0.0725 (4)	0.2158 (6)	0.6384 (2)	0.045 (1)
C(13)	-0.0160 (4)	0.0757 (7)	0.6621 (2)	0.052 (1)
C(14)	-0.0633 (4)	-0.0764 (7)	0.6146 (2)	0.053 (1)
C(15)	0.0389 (4)	-0.1955 (7)	0.5926 (2)	0.055 (2)
C(16)	0.1294 (4)	-0.0577 (8)	0.5699 (2)	0.054 (2)
C(1)	0.2606 (4)	0.2481 (7)	0.5931 (2)	0.049 (1)
C(2)	0.3743 (4)	0.1483 (7)	0.5794 (2)	0.051 (2)
N(2)	0.4404 (3)	0.0615 (5)	0.6362 (1)	0.041 (1)
C(22)	0.5035 (3)	0.2249 (6)	0.6748 (2)	0.047 (1)
C(23)	0.5642 (4)	0.1330 (8)	0.7322 (2)	0.055 (2)
C(24)	0.6500 (4)	-0.0322 (8)	0.7180 (2)	0.058 (2)
C(25)	0.5865 (4)	-0.1944 (7)	0.6782 (2)	0.056 (2)
C(26)	0.5261 (4)	-0.1012 (7)	0.6209 (2)	0.051 (2)
Cl	0.23643 (9)	0.0775 (2)	0.05307 (5)	0.0494 (3)
O(2)	0.2606 (4)	0.1025 (7)	0.1175 (2)	0.089 (2)
O(3)	0.3450 (3)	0.0716 (6)	0.0261 (2)	0.073 (1)
O(4)	0.1761 (5)	-0.1087 (7)	0.0436 (2)	0.108 (2)
O(5)	0.1697 (4)	0.2414 (9)	0.0297 (3)	0.136 (2)
O(W)	0.2233 (3)	0.0885 (5)	0.7910 (1)	0.063 (1)

Table 2. The torsion angles ( $^\circ$ ) of the  $PEtP(NO)_2H^+$  skeleton

The piperidine-ring atoms are labelled N(1)–C(6), and C(1) denotes a bridging atom. Primed atoms belong to the complementary moiety of the cation.

	Ring I	Ring II
O(1)–N(1)–C(2)–C(3)	-64.3 (4)	—
O(1)–N(1)–C(6)–C(5)	63.7 (4)	—
C(1)–N(1)–C(2)–C(3)	179.8 (4)	-176.9 (4)
C(1)–N(1)–C(6)–C(5)	-176.1 (4)	177.7 (4)
C(1')–C(1)–N(1)–O(1)	55.2 (4)	—
C(1')–C(1)–N(1)–C(2)	171.2 (3)	158.7 (4)
C(1')–C(1)–N(1)–C(6)	-66.7 (4)	-77.5 (4)
N(1')–C(1')–C(1)–N(1)	-63.5 (4)	—
C(6)–N(1)–C(2)–C(3)	55.9 (4)	58.3 (4)
N(1)–C(2)–C(3)–C(4)	-58.1 (4)	-57.6 (4)
C(2)–C(3)–C(4)–C(5)	56.8 (4)	56.2 (4)
C(3)–C(4)–C(5)–C(6)	-55.3 (4)	-56.3 (4)
C(4)–C(5)–C(6)–N(1)	55.7 (4)	57.4 (4)
C(5)–C(6)–N(1)–C(2)	-55.0 (4)	-57.9 (4)

& Kosturkiewicz, 1982). Neutron studies of this H bond showed that the proton is, within experimental error, centrally located in the  $O \cdots H \cdots O$  bridge (Jaskólski, Olovsson, Tellgren & Mickiewicz-Wichlacz, 1982). The aim of this study was to establish the conformation of a monoprotonated  $PEtP(NO)$  system, which contains only one *N*-oxide group, and to find out if it also forms an intramolecular H bond.

**Experimental.** Suitable crystals obtained from methanol, crystal  $0.3 \times 0.3 \times 0.4$  mm, Syntex  $P2_1$  diffractometer, cell parameters from least-squares treatment of setting angles of 15 reflexions,  $2\theta:\theta$  profiles measured for 2191 unique reflexions with  $2\theta \leq 115^\circ$  and  $h, k \geq 0$ , profile analysis according to Lehmann & Larsen (1974), no significant variation for 2 standard reflexions, no absorption correction, 1894 observed reflexions with  $I \geq 1.96\sigma(I)$ ; structure solved by Patter-

son and Fourier techniques, full-matrix least squares on  $F$  with  $w = (F_o/3.6)^2$  for  $F_o < 3.6$ ,  $w = (22/F_o)^2$  for  $F_o > 22$  and  $w = 1$  for  $3.6 \leq F_o \leq 22$ , 2 reflexions excluded from final refinement, H atoms located in a  $\Delta F$  map and included as fixed isotropic contribution to  $F_c$ , anisotropic thermal parameters for all non-H atoms,  $R = 0.062$ ,  $R_w = 0.078$ , max.  $\Delta/\sigma = 0.11$ , final  $\Delta F$  map featureless; calculations using original or locally modified (Jaskólski, 1979) Syntex *XTL* programs (Syntex, 1973) on a Nova 1200 minicomputer; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Atomic coordinates are listed in Table 1.\* Bond lengths and angles in the  $PEtP(NO)_2H^+$  cation are given in Fig. 1. Torsion angles are in Table 2. The cation has the *cisoidal* conformation similar to that of  $PEtP(NO)_2H^+$  (Jaskólski, Gdaniec & Kosturkiewicz, 1982). The largest differences between these two systems involve the amino moiety of the present cation [rotation of *ca*  $23^\circ$  around N(2)–C(2)]. On the other hand, the torsion angles in the *N*-oxide moiety of the present cation [*i.e.*  $EtP(NO)_2H^+$ ] are closer to the corresponding values in  $PEtP(NO)_2H^+$ , the main differences being due to *ca*  $12^\circ$  rotation around N(1)–C(1). The conformation around the C(1)–C(2) bridge [ $-63.5(4)^\circ$ ] is closer to the pure *gauche* form than in  $PEtP(NO)_2H^+$  [ $-70.6(3)^\circ$ ]. This indicates that the present six-membered ring with the intramolecular H bridge [C(1)–N(1)–O(1)–H(O1)–N(2)–C(2), see below] is less strained than its seven-membered equivalent in  $PEtP(NO)_2H^+$  [C(1)–N(1)–O(1)–H(O)–O(2)–N(2)–C(2)]. This statement is further supported by the values of the N–C–C angles at the C–C bridge [112.4(3), 111.4(4)°], which are much closer to the tetrahedral angle than the values observed in the *bis-N*-oxide system [117.5(2), 117.4(2)°].

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters,  $ClO_4^-$  bond lengths and angles and H-bonding geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39153 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

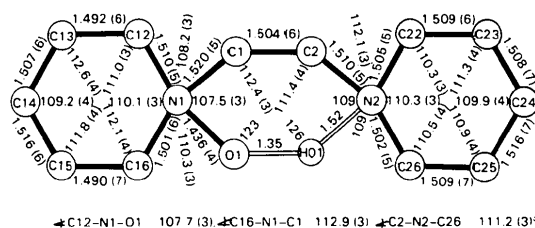


Fig. 1. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the  $PEtP(NO)_2H^+$  cation (carbon H atoms are not displayed).

The *N*-oxide and amino groups of the cation are bridged by an intramolecular O...H...N hydrogen bond, O...N 2.551 (4) Å, which closes a six-membered ring in the central part of the cation. This ring has a sofa conformation with C(1) moved out of the relatively flat N(1)O(1)...H(O1)...N(2)C(2) moiety. According to its geometry, the intramolecular H bond can be classified as very strong (Novak, 1974). The O...H...N angle (126°) is far from linear but it is within the limits acceptable for H bonds (Jaskólski, 1984). According to the H(O1) position determined from a difference-Fourier map (O...H and H...N being respectively 1.35 and 1.52 Å), the H atom is nearly centrally located in the O...H...N bridge and therefore the energy barrier between the O—H...N and O...H—N minima must be relatively low.

The PEtP(NO).H<sup>+</sup> cations are involved in intermolecular H bonds with water molecules. Each water molecule links two adjacent cations *via* HO—H...O(H)—N hydrogen bonds resulting in infinite ...H<sub>2</sub>O...PEtP(NO).H<sup>+</sup>... chains running helically along *b* (Fig. 2). The *N*-oxide O atom is therefore involved in three H bonds: in the intramolecular O...H...N bridge and (as an acceptor) in two bonds with water molecules, 2.782 (4) and 2.837 (4) Å. The water molecule is an acceptor in a weak C(1)—H...O(W) hydrogen bond, 3.383 (5) Å. The donor of this C—H...O hydrogen bond [C(1)] is adjacent to a nitrogen atom bearing partial positive charge [N(1)] in agreement with the observation by Taylor & Kennard (1982) that such C atoms are especially likely to form H bonds.

The mean Cl—O bond length of the perchlorate ion is 1.416 (5) Å. The anion is not involved in H bonding and its O atoms show relatively high thermal motion (Table 1).

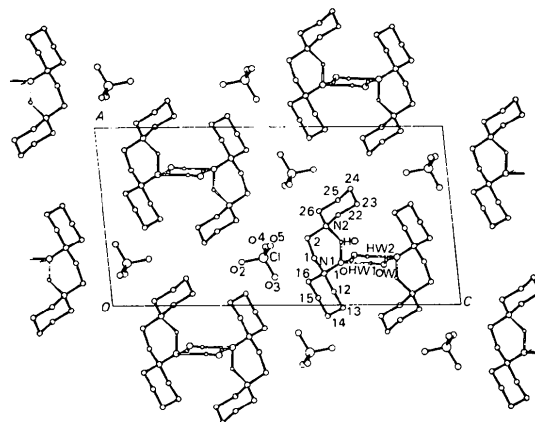


Fig. 2. Projection of the structure down *b*.

#### References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JASKÓLSKI, M. (1979). Thesis, A. Mickiewicz Univ., Poznań.
- JASKÓLSKI, M. (1982). *Pol. J. Chem.* **56**, 187–193.
- JASKÓLSKI, M. (1984). *Pol. J. Chem.* Submitted.
- JASKÓLSKI, M., GDANIEC, M. & KOSTURKIEWICZ, Z. (1982). *Pol. J. Chem.* **56**, 297–305.
- JASKÓLSKI, M., KOSTURKIEWICZ, Z., MICKIEWICZ-WICHLACZ, D. & WIEWIÓROWSKI, M. (1979). *J. Mol. Struct.* **52**, 77–94.
- JASKÓLSKI, M., OLOVSSON, I., TELLGREN, R. & MICKIEWICZ-WICHLACZ, D. (1982). *Acta Cryst.* **B38**, 291–294.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- NOVAK, A. (1974). *Structure and Bonding*, Vol. 18, p. 177. Berlin-Heidelberg-New York: Springer.
- Syntax (1973). *XTL Structure Determination System*. Syntax Analytical Instruments, Cupertino, California.
- TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

*Acta Cryst.* (1984). **C40**, 871–873

### Structure of 1,3-Di-*tert*-butyl-2,2,4,4-tetraisopropylcyclodisilazane, C<sub>20</sub>H<sub>46</sub>N<sub>2</sub>Si<sub>2</sub>

BY WILLIAM CLEGG, MARTIN HAASE, GEORGE M. SHELDRIK AND NORBERT VATER

*Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany*

(Received 21 November 1983; accepted 11 January 1984)

**Abstract.**  $M_r = 370.8$ , monoclinic,  $P2_1/n$ ,  $a = 8.842$  (2),  $b = 15.842$  (3),  $c = 9.266$  (2) Å,  $\beta = 115.89$  (3)°,  $V = 1167.7$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.055$  (1) Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.15$  mm<sup>-1</sup>,  $F(000) = 416$ ,  $T = 291$  K,  $R = 0.041$  for 1670 observed reflections. The molecule has crystallographic inversion symmetry, with a central planar

Si<sub>2</sub>N<sub>2</sub> ring of dimensions Si—N 1.747 (2) and 1.748 (2) Å, Si—N—Si 93.9 (1) and N—Si—N 86.1 (1)°. Consideration of the arrangement of the substituents and comparison with the structures of other cyclodisilazanes suggests that the homologous compound fully substituted with *tert*-butyl groups may be unattainable for steric reasons.