

2,2,6,6-Tetramethyl-4-oxopiperidin-  
ium nitrateV. H. Rodrigues,<sup>a\*</sup> C. Cardoso,<sup>b</sup> J. A. Paixão<sup>a</sup> and  
M. M. R. R. Costa<sup>a</sup><sup>a</sup>CEMEX, Departamento de Física, Faculdade de Ciências e Tecnologia,  
Universidade de Coimbra, P-3004-516 Coimbra, Portugal, and <sup>b</sup>CFC, Departamento  
de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-  
516 Coimbra, Portugal

Correspondence e-mail: vhugo@pollux.fis.uc.pt

Received 9 February 2007

Accepted 19 February 2007

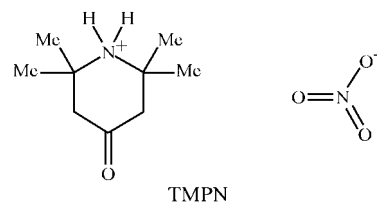
Online 17 March 2007

In the title compound,  $C_9H_{18}NO^+ \cdot NO_3^-$ , the piperidinium ring adopts a slightly deformed chair conformation and the nitrate anion is disordered. The ions are arranged in hydrogen-bonded chains parallel to [001], in which the cations alternate with the anions. The intrachain hydrogen bonds are bifurcated and link the O atoms of the anions to the N atoms of the cations.

## Comment

2,2,6,6-Tetramethyl-4-piperidone (TMP) is a strong organic base widely used as a solvent and as a building block for chemical synthesis in several industries. Moreover, a number of natural products containing the piperidine nucleus have

been found to possess interesting biological and pharmacological activity. We have synthesized 2,2,6,6-tetramethyl-4-oxopiperidinium nitrate, henceforth TMPN, as a side product of an attempt to crystallize sarcosinium nitrate.



Although commonly used in organic synthesis, there are only six crystal structures reported so far in the Cambridge Structural Database (August 2006 update; Allen, 2002) that involve exactly the 2,2,6,6-tetramethyl-4-oxopiperidinium cation. The reported salts include the hexafluorophosphate (Simpson, 1992), trifluoroacetate (Breitung *et al.*, 2003), bis-(pentafluorophenyl)phosphinate (Campana *et al.*, 1998), hydrochloride (Rees & Weiss, 1971) and diethylcarbamoylmethyl phosphonate (Conary *et al.*, 1993), and the mixed cation salt bis([1,8-bis[(diphenylphosphino)methyl]naphthalene]xylylnitrilepalladium) bis(2,2,6,6-tetramethylpiperidonium) tetrakis(hexafluorophosphate) (Yamamoto *et al.*, 2001).

The chemical path that led to the formation of the title compound probably consists of an amination, by  $NH_3$  generated by an equilibrium of  $NH_4NO_3$ , of a diol arising from the trimerization of acetone, followed by a ring closure, as depicted in Fig. 1 (Yamamoto *et al.*, 2001).

The cation has typical angles and distances, and a slightly distorted chair conformation (Fig. 2). The ring-puckering parameters are  $\varphi = -123(2)^\circ$ ,  $\theta = 5.5(2)^\circ$  and  $Q_T = 0.510(2)\text{Å}$ , corresponding to a chair conformation with only a small distortion towards a half-boat conformation; one aspect

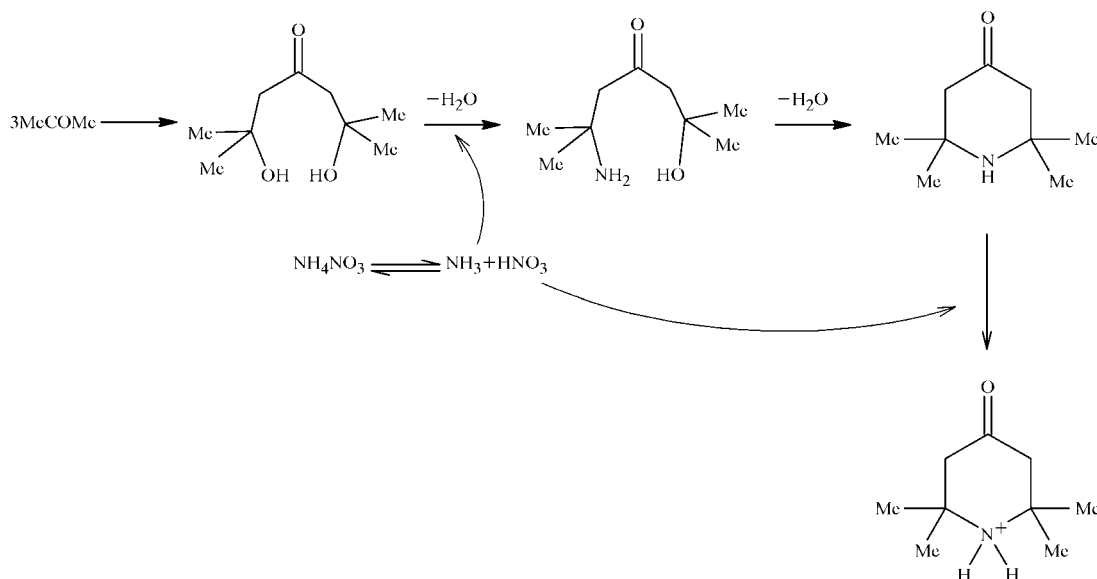


Figure 1

Trimerization of acetone resulting in a diol which suffers amination of  $NH_3$ . The ammonia molecule originates from the equilibrium of  $NH_4^+$  cations in solution. Protonation of the amide group follows the ring closure (Yamamoto *et al.*, 2001).

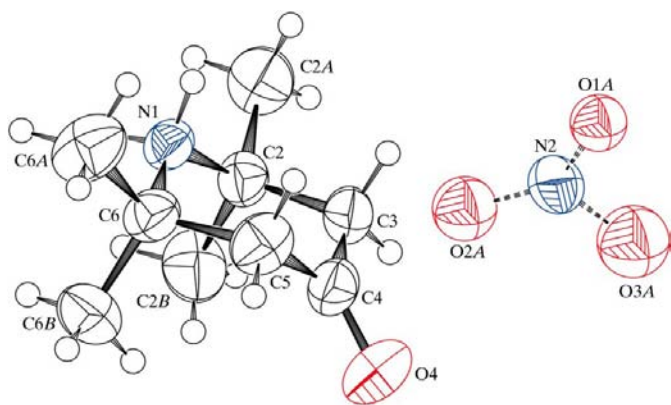
of this distortion is the different distances of atoms N1 and C4 from the plane defined by atoms C2, C3, C5 and C6, the first distance being 0.552 (3) Å and the second –0.606 (4) Å. A deviation from an ideal cyclohexane chair conformation should be expected taking into account the presence of a heteroatom in the ring and the planarity at C4; the latter should have a greater influence on the distortion of the ring, leading to an increase of the C3–C4–C5 angle from the ideal tetrahedral value towards 120°. Indeed the reported structures containing TMP (protonated, unprotonated and N1-substituted) show a C3–C4–C5 angle larger than 109.47° but smaller than 120°, with a mean value of 115 (2)°. The C2–N1–C6 angle also increases, being in all cases close to 120°, with a mean value of 121 (2)°, which is rather uncommon for four-connected nitrogen. The arrangement of the methyl groups with respect to the ring plane is similar to that in many other TMP compounds. Two of the methyl atoms, C2B and C6B, are in an axial position with respect to the ring mean plane; atom C2A is in a bisectonal, nearly equatorial, position, whereas atom C3A is equatorial but nearly bisectonal.

The geometry of TMP was optimized computationally using the *GAMESS* program (Schmidt *et al.*, 1993) for comparison purposes. The calculations were performed for both the neutral and the protonated TMP molecules in vacuum. A 6–31G base with *p* and *d* polarization functions was used. The calculations were performed within the Hartree–Fock approximation. The geometries determined for the neutral and protonated molecules are very similar; the changes in bond lengths are within 0.01–0.08 Å and bond-angle differences are at most 2°. There is a clear trend in the calculated geometry changes when going from neutral to protonated TMP; the N–C and C–C intra-ring bonds all increase, whereas the C–O distance decreases, showing a stabilization of the ketone group. The distances of the substituent methyl groups from their parent C atoms of the ring (atoms C2 and C6) are slightly different in the neutral molecule and become equal in the protonated form. The puckering in the calculated rings is similar, corresponding to a slightly deformed chair

conformation. All geometric features obtained from the calculations for the gas phase agree with the experimental geometry of TMP in TMPN; however, the agreement of the calculated parameters of the protonated molecule with our experiment is slightly better, which further confirms the positive charge state of TMP in the title compound.

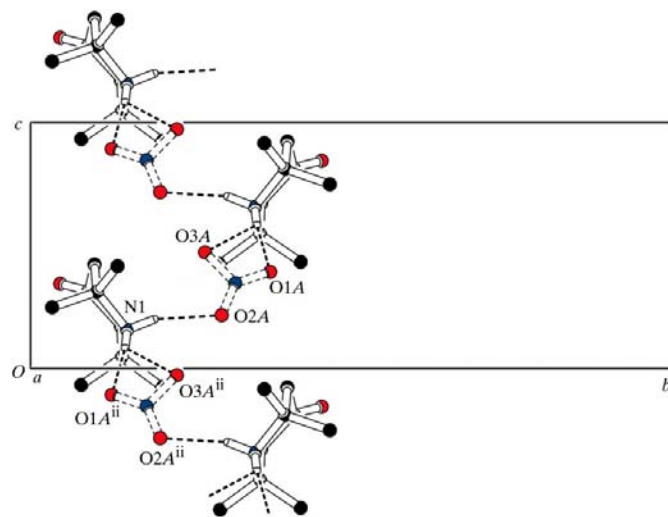
The O atoms of the disordered nitrate anion were modelled using four sets of sites. The refinement of the disordered model was only possible with appropriate restraints that ensured an average ideal trigonal geometry of the anion in each case, and the O-atom displacement tensors were made isotropic. Nevertheless, such a procedure led to a significant improvement of the final quality factors of the refinement; a final occupation ratio of roughly 2:1:1 for the two different positions was obtained.

The cations and anions of the title compound form zigzag chains along the *c* axis (Fig. 3) with graph-set symbol  $C_2^2(6)$  (Grell *et al.*, 1999). There is also a small ring motif of the  $R_1^2(4)$  type embedded in the chains. The chains are bonded *via* strong hydrogen bonds (Table 1) in which atom N1 in the cation is the donor and all three O atoms of the anion (major component) act as acceptors. Atom H1A is involved in two hydrogen bonds with different acceptor O atoms in a bifurcated hydrogen bond. Only two of the six structures containing the TMP cation already published exhibit hydrogen-bonded chains, namely the trifluoroacetate salt, also of the  $C_2^2(6)$  type, and the hexafluorophosphate salt, of the  $C(6)$  type. Three of the reported structures that do not have chains show large rings of graph-set motifs  $R_8^4(16)$ ,  $R_4^4(8)$  and  $R_4^4(12)$ , *viz.* the chloride, the diethylcarbamoylmethyl phosphonate and the bis(pentafluorophenyl)phosphinate salt, respectively. Bis([1,8-bis[(diphenylphosphino)methyl]naphthalene]xylylnitrilepalladium) bis(2,2,6,6-tetramethylpiperidonium) tetrakis(hexafluorophosphate) shows only small  $R_1^2(4)$  rings.



**Figure 2**

An *ORTEP* (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Only one orientation of the disordered nitro group is shown.



**Figure 3**

The packing of molecules, showing a zigzag chain running along the *c* axis and the intrachain hydrogen-bonding scheme. For clarity, all H atoms not involved in hydrogen bonds have been omitted, as have the minor components of the disordered anions. [Symmetry code: (ii)  $x, y + \frac{1}{2}, z - \frac{1}{2}$ ]

## Experimental

Equimolar amounts of sarcosine and ammonium nitrate were dissolved in a concentrated aqueous ammonia solution. Acetone was added to induce precipitation. The resulting clear homogeneous colourless solution was then heated to boiling for 15 min. A red colour started to develop slowly during the heating procedure and turned to dark red after a few hours of cooling to room temperature. The entire procedure was repeated without sarcosine with the same results. After a few days of slow evaporation, small plate-like crystals of the title compound started to grow.

### Crystal data

$C_9H_{18}NO^+ \cdot NO_3^-$	$V = 1158.38 (15) \text{ \AA}^3$
$M_r = 218.25$	$Z = 4$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 7.7170 (4) \text{ \AA}$	$\mu = 0.82 \text{ mm}^{-1}$
$b = 19.7883 (8) \text{ \AA}$	$T = 290 (2) \text{ K}$
$c = 9.6468 (8) \text{ \AA}$	$0.3 \times 0.2 \times 0.05 \text{ mm}$
$\beta = 128.155 (5)^\circ$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	2301 independent reflections
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	1474 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.854$ , $T_{\max} = 0.959$	$R_{\text{int}} = 0.060$
3417 measured reflections	3 standard reflections
	frequency: 180 min
	intensity decay: 5%

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	167 parameters
$wR(F^2) = 0.191$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
2301 reflections	$\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O1A^i$	0.90	2.00	2.886 (7)	167
$N1-H1A \cdots O3A^i$	0.90	2.38	3.066 (9)	133
$N1-H1B \cdots O2A$	0.90	2.09	2.955 (9)	162

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

H atoms were located in a difference Fourier map and were refined as riding [ $C-H = 0.96$  or  $0.97 \text{ \AA}$  and  $N-H = 0.90 \text{ \AA}$ ;  $U_{\text{iso}}(H) =$

$1.2U_{\text{eq}}(C,N)$  or  $1.5U_{\text{eq}}(C)$ ]. The O atoms of the four components of the disordered nitrate ion were subject to appropriate restraints to ensure an average trigonal-planar geometry and refined isotropically. Examination of the crystal structure with *PLATON* (Spek, 2003) showed that there are no solvent-accessible voids in the crystal structure. Theoretical calculations were performed using *GAMESS* (Schmidt *et al.*, 1993).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PLATON* (Spek, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

This work was supported by Fundação para a Ciência e a Tecnologia (FCT).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3091). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Breitung, S., Lerner, H.-W. & Bolte, M. (2003). *Acta Cryst.* **E59**, o445–o446.
- Campana, C. F., Oliver, K. W., Rettig, S. J., Thompson, R. C., Trotter, J. & Xia, S. (1998). *Acta Cryst.* **C54**, 99–101.
- Conary, S. C., McCabe, D. J., Cudde, L. J., Duesler, E. N. & Paine, R. T. (1993). *Inorg. Chim. Acta*, **207**, 213–222.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Grell, J., Bernstein, J. & Tinhofer, G. (1999). *Acta Cryst.* **B55**, 1030–1043.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rees, B. & Weiss, R. (1971). *Acta Cryst.* **B27**, 932–940.
- Schmidt, M. W., Baldrige, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S. J., Windus, T. L., Dupuis, M. & Montgomery, J. A. (1993). *J. Comput. Chem.* **14**, 1347–1363.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Simpson, S. J. (1992). *Acta Cryst.* **C48**, 1137–1138.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Yamamoto, Y., Fukui, Y., Matsubara, K., Takeshima, H., Miyauchi, F., Tanase, T. & Yamamoto, G. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1773–1781.