| | | | | |
|---|---|---|---|---|
| N1—C8 | 1.478 (4) | 1.481 (2) | 1.474 (2) | 1.475 (5) |
| N1*A*—C8*A* | | | 1.477 (2) | 1.476 (5) |
| C3—C4 | 1.370 (5) | 1.371 (2) | 1.370 (2) | 1.373 (5) |
| C3*A*—C4*A* | | | 1.371 (2) | 1.367 (5) |
| C4—C5 | 1.420 (5) | 1.439 (2) | 1.435 (2) | 1.433 (5) |
| C4*A*—C5*A* | | | 1.438 (2) | 1.437 (5) |

† Two independent molecules.

Table 2. *Hydrogen-bonding geometry (Å, °) for compounds (1), (2), (3) and (4)*

| Compound | *D*—H···*A* | *D*···*A* | H···*A* | *D*—H···*A* |
|---|---|---|---|---|
| (1) | O1—H1···O2$^{i}$ | 2.700 (4) | 1.919 | 142.4 |
| (2) | O1—H1···O2$^{ii}$ | 2.692 (1) | 1.802 | 145.7 |
| (3) | O1—H1···O2*A* | 2.699 (2) | 1.919 | 150.7 |
| | O1*A*—H1*A*···O2 | 2.639 (2) | 1.815 | 154.2 |
| (4) | O1—H1···O2*A* | 2.582 (3) | 1.468 | 167.3 |
| | O1*A*—H1*A*···O2 | 2.640 (4) | 1.744 | 145.2 |

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, 1 - y, -z$.

For all four structures, the bridging H atoms were located as the highest residual electron density when all other atoms were included in the refinement. For the final refinement cycles, the positional parameters of the bridging H atoms and those of the calculated C—H atoms were constrained using a riding model.

For all compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1996); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1028). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). C**54**, 2015-2019

# Tris{[tris(2-hydroxymethyl)methyl]ammonium} D-3-Phosphoglycerate at 150 K and Tris(cyclohexylammonium) D-3-Phosphoglycerate Ethanol Solvate at 85 K

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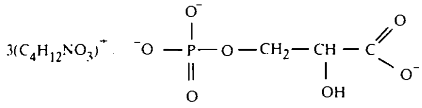
## Abstract

The structures of the D-3-phosphoglycerate trianion in the tris{[tris(2-hydroxymethyl)methyl]ammonium} salt, $3C_4H_{12}NO_3^+.C_3H_4O_7P^{3-}$, (I), and in the tris(cyclohexylammonium) ethanol solvate, $3C_6H_{14}N^+.C_3H_4O_7P^{3-}.C_2H_5OH$, (II), have been determined by X-ray analyses at 150 and 85 K, respectively. A notable feature of (I) is the shortest P—O(ester) bond [1.607 (2) Å] found so far for the completely ionized phosphate ester group. In contrast, in (II), this bond length is 1.627 (2) Å, similar to that observed in doubly ionized phosphate ester groups. In (II), the carboxylate group is twisted by −23.5 (4)° relative to the α-hydroxyl group, as indicated by the O1—C1—C2—O2 torsion angle, whereas in (I), the O2—C2—C1—O1 system is almost planar. Both crystal structures are stabilized by hydrogen bonds utilizing all N and O atoms.

## Comment

The investigation presented in this paper is part of our systematic studies of D-3-phosphoglycerates (3-PGA) with different ionization states (Jerzykiewicz & Lis, 1997). In previous papers, the structures of mono-ionized (Lis & Jerzykiewicz, 1995) and doubly ionized 3-PGA anions (Lis & Jerzykiewicz, 1996; Jerzykiewicz & Lis, 1997) were reported. We now describe the crystal structures of the completely ionized 3-PGA anion in the tris{[tris(2-hydroxymethyl)methyl]ammonium} salt, (I), and in the tris(cyclohexylammonium) ethanol solvate, (II).



(I)

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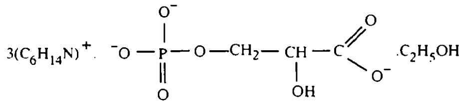

$$3(C_6H_{14}N)^+ \cdot {}^-O-\underset{\underset{O}{\|}}{\overset{\overset{O^-}{|}}{P}}-O-CH_2-\underset{\underset{OH}{|}}{CH}-C\!\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix} \cdot C_2H_5OH$$

(II)

Crystals of (I) consist of tris[(2-hydroxymethyl)methyl]ammonium cations and D-3-phosphglycerate anions (Fig. 1). Crystals of (II) are built up from cyclohexylammonium cations, D-3-phosphoglycerate anions (Fig. 2) and ethanol molecules of solvation. The main structural feature of (I) is the shortest P—O(ester) bond length out of those found up to now in doubly ionized monophosphate esters (Starynowicz, 1986; Starynowicz *et al.*, 1986; Jerzykiewicz, 1995). The bond distance of 1.607 (2) Å observed in (I) is more characteristic of mono-ionized phosphate groups [mean value 1.605 (3) Å] than doubly ionized phosphate esters [mean value 1.624 (3) Å; Jerzykiewicz, 1995]. Such a short ester bond in this completely ionized phosphate group may be explained by the fact that terminal O atoms of the phosphate group are involved in eight hydrogen bonds. Two O atoms (O31 and O32) of the phosphate group form three hydrogen bonds whereas the third one (O33) participates in two hydrogen-bond bridges (Table 2). In structure (II), which is similar to 3-PGA anion structures described previously, as well as many monophosphate esters, the number of hydrogen bonds in which O atoms of the phosphate group participate is smaller. Such a large increase of hydrogen bonding in (I) probably causes changes of electron density, which is reflected in shortering of the P—O(ester) bond in (I). Thus, it may be said that the ester bond length does not depend mainly on the formal ionization state of the phosphate group, but on the charge density localized on terminal O atoms of the phosphate group. Other geometrical parameters of the phosphate group in (I), as well as in (II), do not differ significantly from those found in previously described phosphoglycerates (Jerzykiewicz, 1995). In both salts, one of the terminal O atoms (O31) is localized in a *trans* position with respect to the C3 atom, and the orientation of the phosphate group is antiperiplanar with respect to the C-atom chain, as is indicated by the O31—P—O3—C3 and P—O3—C3—C2 torsion angles (Table 1).

The basic difference between the glycerate residues in the two structures is the orientation of the carboxylate group with respect to the O2 atom. As in other structures of 3-PGA (Jerzykiewicz & Lis, 1994, 1997; Lis & Jerzykiewicz, 1995, 1996), in (I), the O2—C2—C1—O1 system is almost planar [O2—C2—C1—O1 −1.9 (3)°], whereas in (II), the O2 atom does not lie in the plane of the carboxylate group [O2—C2—C1—O1 −23.5 (4)°]. In each salt, the carboxylate group is partially eclipsed with respect to the glycerate residue, as indicated by the O1—C1—C2—C3 torsion angles (Tables 1 and 3).

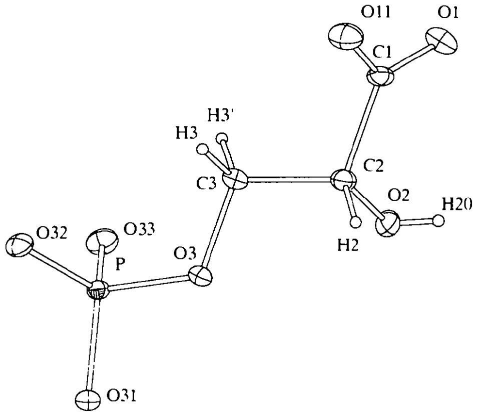

Fig. 1. The structure and numbering scheme of the 3-PGA trianion in (I). Displacement ellipsoids are plotted at the 50% probability level.

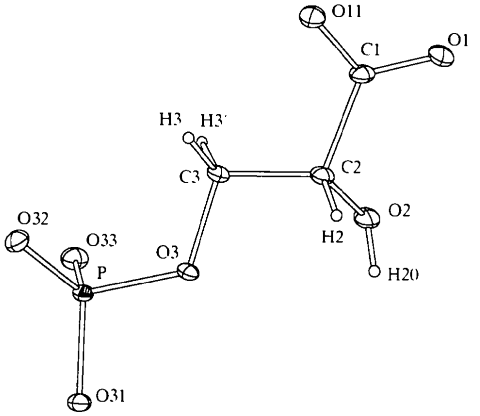

Fig. 2. The structure and numbering scheme of the 3-PGA trianion in (II). Displacement ellipsoids are plotted at the 50% probability level.

The three crystallographically independent tris[(2-hydroxymethyl)methyl]ammonium cations (TRISH$^+$) have different conformations (Fig. 3). The numeric parameters of the TRISH$^+$ cations are very similar to those found in analogous crystals (Castellari & Ottani, 1997; Rudman *et al.*, 1983). The C—N bond lengths of 1.490 (3)–1.499 (3) Å are longer than in the non-ionized TRIS molecule, where this distance is 1.471 (2) Å (Castellari & Ottani, 1997). The C—O bond lengths are comparable with those found in other TRIS and TRISH$^+$ moieties.

The crystal packing of (I) (Fig. 3) is determined by the hydrogen bonds between TRISH$^+$ cations and 3-PGA anions, as well as by hydrogen bridges in which only TRISH$^+$ cations participate, with their $NH_3^+$ groups as donors and OH groups as both donors and acceptors.

The crystal packing of (II) is determined by hydrophilic regions filled with 3-PGA anions, ammonium groups of the cyclohexylammonium cations and hydroxy groups of the ethanol molecules; surrounding hydrophobic regions are formed by cyclohexyl rings

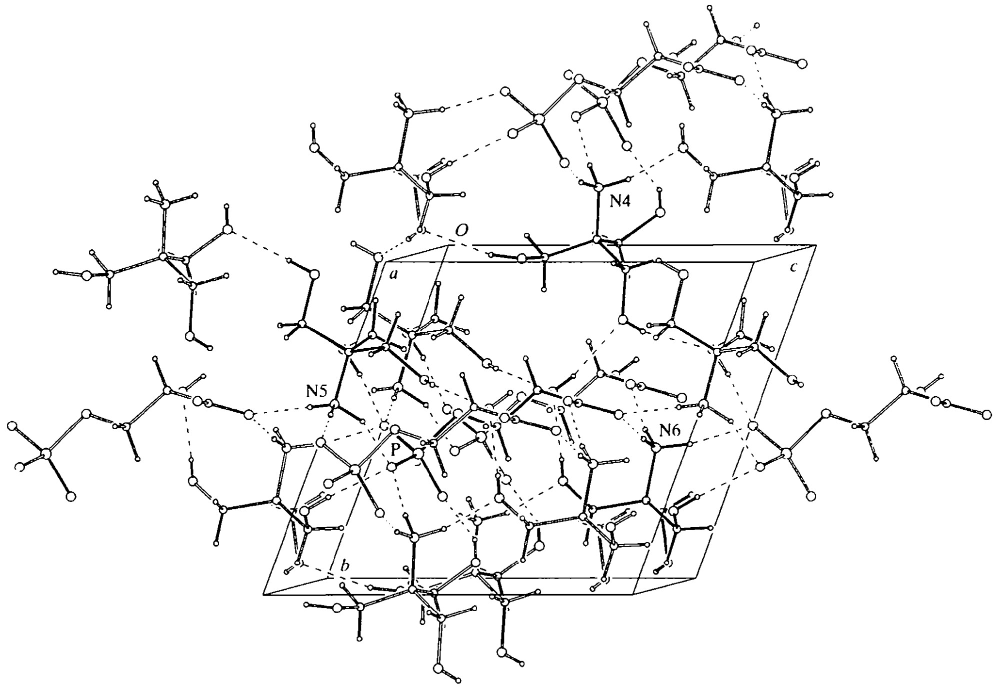

Fig. 3. The packing arrangement in the crystal of (I).

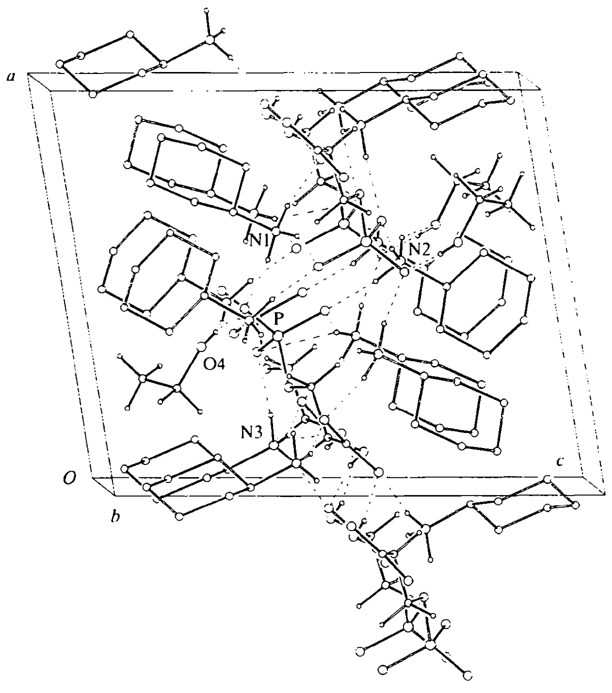

Fig. 4. The packing arrangement in the crystal of (II).

and ethyl groups of ethanol molecules (Fig. 4). The 3-PGA anions are mainly involved in hydrogen bonding with cyclohexylammonium cations. Moreover, 3-PGA anions are linked directly to one another through hydrogen bridges between the hydroxy groups (O2) and O atoms of the carboxylate groups. The ethanol molecule is a donor in a short hydrogen bond to the phosphate group and an acceptor in a weak hydrogen bond with the cyclohexylammonium cation.

## Experimental

Crystals of (I) were grown by slow concentration of aqueous solutions containing a 3:1 molar ratio of tris(hydroxymethyl)(amino)methane (TRIS) and D-3-phosphoglyceric acid (Jerzykiewicz, 1995). Crystals of (II) were obtained by slow diffusion of ethanol into a methanol solution of the commercially available compound (Sigma).

### Compound (I)

*Crystal data*

$3C_4H_{12}NO_3^+.C_3H_4O_7P^{3-}$
$M_r = 549.47$
Triclinic
$P1$
$a = 6.416\,(3)$ Å
$b = 10.109\,(4)$ Å
$c = 10.200\,(4)$ Å
$\alpha = 109.80\,(4)°$
$\beta = 103.93\,(4)°$
$\gamma = 95.95\,(3)°$
$V = 591.6\,(4)$ Å$^3$
$Z = 1$
$D_x = 1.542$ Mg m$^{-3}$
$D_m = 1.514$ Mg m$^{-3}$
$D_m$ measured by flotation in $CCl_4/CHCl_3$ at room temperature

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 62 reflections
$\theta = 10.5–16.5°$
$\mu = 0.201$ mm$^{-1}$
$T = 150\,(2)$ K
Block
0.5 × 0.3 × 0.2 mm
Colourless

*Data collection*

Kuma KM-4 diffractometer with Oxford Cryosystems Cryostream Cooler
Profile data from $\theta/2\theta$ scans
Absorption correction: none
3418 measured reflections
3418 independent reflections
2991 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 30°$
$h = 0 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: 2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.082$
$S = 1.128$
3418 reflections
382 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.021P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.002$
$\Delta\rho_{\max} = 0.58$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.31$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.06 (8)

Table 1. *Selected geometric parameters (Å, °) for (I)*

| | | | |
|---|---|---|---|
| P—O31 | 1.523 (2) | C4—C47 | 1.541 (3) |
| P—O32 | 1.528 (2) | C5—C55 | 1.527 (3) |
| P—O33 | 1.505 (2) | C5—C56 | 1.529 (3) |
| P—O3 | 1.607 (2) | C5—C57 | 1.533 (3) |
| O1—C1 | 1.258 (3) | C6—C65 | 1.522 (3) |
| O11—C1 | 1.241 (3) | C6—C66 | 1.536 (3) |
| O2—C2 | 1.428 (3) | C45—O45 | 1.417 (3) |
| O3—C3 | 1.435 (3) | C46—O46 | 1.415 (3) |
| C1—C2 | 1.543 (3) | C47—O47 | 1.427 (3) |
| C2—C3 | 1.510 (3) | C55—O55 | 1.420 (3) |
| N4—C4 | 1.495 (3) | C56—O56 | 1.420 (3) |
| N5—C5 | 1.490 (3) | C57—O57 | 1.435 (3) |
| N6—C6 | 1.499 (3) | C65—O65 | 1.425 (3) |
| C4—C45 | 1.526 (3) | C66—O66 | 1.411 (3) |
| C4—C46 | 1.528 (3) | | |
| O31—P—O32 | 110.36 (9) | O11—C1—O1 | 126.6 (2) |
| O31—P—O33 | 115.18 (10) | O11—C1—C2 | 115.8 (2) |
| O32—P—O33 | 111.72 (10) | O1—C1—C2 | 117.6 (2) |
| O31—P—O3 | 102.23 (9) | O2—C2—C3 | 108.0 (2) |
| O32—P—O3 | 107.91 (9) | O2—C2—C1 | 113.3 (2) |
| O33—P—O3 | 108.78 (10) | C3—C2—C1 | 108.5 (2) |
| C3—O3—P | 118.46 (14) | O3—C3—C2 | 108.3 (2) |
| C3—O3—P—O31 | 179.8 (2) | C1—C2—C3—O3 | −177.2 (2) |
| C3—O3—P—O32 | −63.8 (2) | N4—C4—C45—O45 | 64.5 (2) |
| C3—O3—P—O33 | 57.6 (2) | N4—C4—C46—O46 | −175.2 (2) |
| P—O3—C3—C2 | −161.0 (2) | N4—C4—C47—O47 | −39.6 (2) |
| O2—C2—C3—O3 | 59.6 (2) | N5—C5—C55—O55 | −53.7 (2) |
| O1—C1—C2—O2 | 1.9 (3) | N5—C5—C56—O56 | −173.9 (2) |
| O11—C1—C2—O2 | −178.1 (2) | N5—C5—C57—O57 | −47.9 (2) |
| O1—C1—C2—C3 | −118.0 (2) | N6—C6—C65—O65 | −59.3 (2) |
| O11—C1—C2—C3 | 61.9 (2) | N6—C6—C66—O66 | −47.7 (2) |

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H20···O46 | 0.72 (4) | 2.08 (4) | 2.788 (3) | 170 (4) |
| N4—H41···O65$^{\rm i}$ | 0.93 (4) | 2.04 (4) | 2.925 (3) | 158 (3) |
| N4—H42···O33$^{\rm i}$ | 0.92 (4) | 1.84 (4) | 2.724 (3) | 160 (4) |
| N4—H43···O32$^{\rm ii}$ | 0.90 (4) | 1.82 (4) | 2.717 (3) | 174 (4) |
| O45—H45···O67$^{\rm iii}$ | 0.79 (5) | 2.19 (5) | 2.974 (4) | 168 (5) |
| O45—H45···O68$^{\rm iii}$ | 0.79 (5) | 2.28 (5) | 2.824 (10) | 126 (4) |
| O46—H46···O57$^{\rm iv}$ | 0.71 (5) | 2.05 (5) | 2.735 (3) | 163 (5) |
| O47—H47···O33$^{\rm ii}$ | 0.75 (5) | 1.93 (4) | 2.634 (3) | 156 (4) |
| N5—H51···O1$^{\rm v}$ | 0.79 (4) | 2.01 (4) | 2.792 (3) | 176 (4) |
| N5—H52···O31$^{\rm vi}$ | 0.83 (4) | 1.91 (4) | 2.740 (3) | 178 (4) |
| N5—H53···O32 | 1.01 (4) | 1.80 (4) | 2.757 (3) | 157 (3) |
| O55—H55···O2$^{\rm vi}$ | 0.72 (5) | 2.22 (5) | 2.888 (3) | 154 (5) |
| O56—H56···O47$^{\rm vii}$ | 0.77 (5) | 1.92 (5) | 2.686 (3) | 175 (5) |
| O57—H57···O31 | 0.95 (4) | 1.78 (4) | 2.728 (3) | 173 (4) |
| N6—H61···O1 | 0.85 (4) | 1.97 (4) | 2.819 (3) | 176 (4) |
| N6—H62···O11$^{\rm viii}$ | 0.84 (4) | 1.92 (4) | 2.753 (3) | 171 (4) |
| N6—H63···O31$^{\rm iv}$ | 0.92 (4) | 1.85 (4) | 2.764 (3) | 169 (4) |
| O65—H65···O2 | 0.72 (5) | 2.14 (5) | 2.864 (3) | 176 (5) |
| O66—H66···O32$^{\rm iv}$ | 0.79 (5) | 1.92 (5) | 2.714 (3) | 175 (4) |
| O67—H67···O56$^{\rm ix}$ | 0.80 (6) | 1.99 (6) | 2.787 (3) | 175 (5) |
| O68—H68···O66$^{\rm viii}$ | 0.80 (7) | 1.98 (18) | 2.546 (10) | 127 (19) |

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 + x, 1 + y, z$; (iii) $x, 1 + y, 1 + z$; (iv) $x, y, z - 1$; (v) $x, y, 1 + z$; (vi) $x - 1, y, z$; (vii) $x - 1, y, 1 + z$; (viii) $1 + x, y, z$; (ix) $1 + x, y - 1, z - 1$.

**Compound (II)**

*Crystal data*

$3C_6H_{14}N^+.C_3H_4O_7P^{3-}.C_2H_6O$
$M_r = 529.65$
Monoclinic
$P2_1$
$a = 11.501$ (9) Å
$b = 9.122$ (7) Å
$c = 13.859$ (12) Å
$\beta = 99.22$ (6)°
$V = 1435$ (2) Å$^3$
$Z = 2$
$D_x = 1.226$ (3) Mg m$^{-3}$
$D_m = 1.22$ Mg m$^{-3}$
$D_m$ measured by flotation in $CHCl_3/C_6H_5Cl$ at room temperature

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 8$–12°
$\mu = 0.143$ mm$^{-1}$
$T = 85$ (2) K
Plate
0.50 × 0.35 × 0.25 mm
Colourless

*Data collection*

Kuma KM-4 diffractometer with Oxford Cryosystems Cryostream Cooler
Profile data from $\theta/2\theta$ scans
Absorption correction: none
8124 measured reflections
7587 independent reflections
5752 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\max} = 30°$
$h = -16 \rightarrow 15$
$k = -2 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: −10%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.143$
$S = 1.052$
7587 reflections
400 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.081P)^2 + 0.43P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.048$
$\Delta\rho_{\max} = 0.50$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.44$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (11)

Table 3. *Selected geometric parameters (Å, °) for (II)*

| | | | |
|---|---|---|---|
| P—O31 | 1.522 (2) | C2—C3 | 1.517 (4) |
| P—O32 | 1.520 (2) | O2—C2 | 1.421 (4) |
| P—O33 | 1.520 (2) | C1—C2 | 1.541 (4) |
| P—O3 | 1.627 (2) | O1—C1 | 1.247 (4) |
| O3—C3 | 1.433 (3) | O11—C1 | 1.266 (4) |
| O31—P—O32 | 114.32 (12) | O3—C3—C2 | 106.7 (2) |
| O31—P—O33 | 111.87 (12) | O2—C2—C3 | 111.1 (2) |

| | | | |
|---|---|---|---|
| O32—P—O33 | 112.77 (12) | O2—C2—C1 | 109.3 (2) |
| O31—P—O3 | 101.53 (11) | C3—C2—C1 | 112.3 (2) |
| O32—P—O3 | 107.37 (12) | O1—C1—O11 | 125.2 (3) |
| O33—P—O3 | 108.07 (12) | O1—C1—C2 | 118.6 (3) |
| C3—O3—P | 117.6 (2) | O11—C1—C2 | 116.2 (3) |
| C3—O3—P—O31 | 178.0 (2) | O1—C1—C2—O2 | −23.5 (4) |
| C3—O3—P—O32 | −61.7 (2) | O11—C1—C2—O2 | 159.9 (2) |
| C3—O3—P—O33 | 60.2 (2) | O1—C1—C2—C3 | −147.3 (3) |
| P—O3—C3—C2 | −166.7 (2) | O11—C1—C2—C3 | 36.1 (3) |
| O2—C2—C3—O3 | 65.8 (3) | C1—C2—C3—O3 | −171.4 (2) |

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H20···O1$^{i}$ | 0.79 (5) | 1.96 (5) | 2.728 (4) | 164 (4) |
| N1—H11N···O32 | 0.88 (4) | 1.78 (4) | 2.651 (4) | 171 (4) |
| N1—H12N···O11$^{ii}$ | 0.90 (4) | 2.03 (4) | 2.915 (4) | 169 (3) |
| N1—H13N···O33$^{iii}$ | 0.79 (5) | 2.17 (6) | 2.817 (4) | 140 (5) |
| N1—H13N···O31$^{iii}$ | 0.79 (5) | 2.47 (5) | 3.190 (4) | 151 (5) |
| N2—H21N···O31$^{iii}$ | 0.84 (5) | 1.91 (5) | 2.745 (4) | 171 (4) |
| N2—H22N···O33 | 0.85 (5) | 1.90 (5) | 2.722 (4) | 163 (5) |
| N2—H23N···O4$^{ii}$ | 0.87 (4) | 2.20 (4) | 2.933 (4) | 142 (4) |
| N3—H31N···O1$^{i}$ | 0.87 (4) | 1.95 (4) | 2.785 (4) | 161 (4) |
| N3—H32N···O11$^{iv}$ | 0.88 (4) | 1.95 (4) | 2.801 (4) | 164 (4) |
| N3—H33N···O31 | 0.93 (4) | 1.86 (4) | 2.754 (4) | 162 (4) |
| N3—H33N···O3 | 0.93 (4) | 2.55 (4) | 3.247 (4) | 133 (3) |
| O4—H4···O32 | 0.89 (5) | 1.81 (5) | 2.691 (4) | 169 (4) |

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

For both crystals, the space group and approximate unit-cell parameters were determined from oscillation and Weissenberg photographs. A crystal of (I) was mounted on the diffractometer and cooled slowly to 150 K. After refinement, an additional significant peak was found on a difference map near one of the hydroxy groups of one of the [tris(hydroxymethyl)methyl]-ammonium cations. It was admitted as a partially disordered $-CH_2OH$ group. The structure of (II) was initially measured at 293 K and solved by direct methods. The displacement parameters for some of the C atoms of the cyclohexylammonium rings showed large values, suggesting disorder. Therefore, a second data set of reflections was collected at 85 K. Based on the new data set, the structure was refined again. In the case of (II), the standard reflections decreased in intensity by approximately 10% over the period of data collection; the data were therefore rescaled using the intensities of the standards. For both compounds, the absolute configuration was based on the known stereochemistry at C2. The C-bound H atoms were included in geometrically calculated positions for both compounds and the remaining H atoms were found from difference maps and refined isotropically. The crystal data for (II) at 293 (2) K are: $a$ = 11.695 (7), $b$ = 9.197 (8), $c$ = 14.034 (9) Å, $\beta$ = 99.13 (5)°, $V$ = 1490.4 (3) Å$^3$ and $D_x$ = 1.180 (2) Mg m$^{-3}$.

For both compounds, data collection: *Kuma KM-4 User's Guide* (Kuma Diffraction, 1989); cell refinement: *Kuma KM-4 User's Guide*; data reduction: *Kuma KM-4 User's Guide*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1281). Services for accessing these data are described at the back of the journal.

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# *S*-Benzylisothiouronium Chloride

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## Abstract

The C—N bonds in $C_8H_{11}N_2S^+.Cl^-$, a potent inhibitor of human nitric oxide synthase (HNOS), were found to be similar in length, indicating delocalization over the N—C—N fragment. The delocalization extends to the central C—S bond, indicating a structure more similar to a guanidine system than an amidinium one.

## Comment

Structural studies of amidines and amidinium salts continue to attract attention (Barker *et al.*, 1997; Barker & Kilner, 1994; Edelmann, 1994; Dehnicke, 1990) because of their catalytic, pharmaceutical and biological importance, and their coordination chemistry. The study of the title compound, (I), was carried out to furnish

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