

2375 measured reflections
2375 independent reflections
1578 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R(F) = 0.050$
 $wR(F^2) = 0.094$
 $S = 1.13$
2375 reflections
267 parameters
All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.729P]$
where $P = (F_o^2 + 2F_c^2)/3$

2 standard reflections
frequency: 60 min
intensity decay: <2%

$(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
SHELXL93 (Sheldrick,
1993)

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989).
Cell refinement: *CAD-4 Software*. Data reduction: *DATRD2*
in *NRCVAX* (Gabe, Le Page, White & Lee, 1987).
Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990).
Program(s) used to refine structure: *SHELXL93* (Sheldrick,
1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRC-*
VAX. Software used to prepare material for publication:
SHELXL93.

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for providing financial support and supplying the com-
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ing the facility to work.

Lists of atomic coordinates, displacement parameters, structure factors
and complete geometry have been deposited with the IUCr (Reference:
BK1267). Copies may be obtained through The Managing Editor,
International Union of Crystallography, 5 Abbey Square, Chester CH1
2HU, England.

Table 1. Selected geometric parameters (\AA , $^\circ$)

C(1)—C(6)	1.368 (6)	C(9)—C(11)	1.510 (4)
C(1)—C(2)	1.387 (5)	C(11)—C(16)	1.378 (4)
C(2)—C(3)	1.391 (4)	C(11)—C(12)	1.380 (4)
C(2)—S(7)	1.758 (3)	C(12)—C(13)	1.378 (4)
C(3)—C(4)	1.374 (4)	C(13)—C(14)	1.376 (4)
C(3)—N(21)	1.402 (4)	C(14)—C(15)	1.375 (4)
C(4)—C(5)	1.375 (5)	C(14)—O(17)	1.375 (3)
C(5)—C(6)	1.374 (5)	C(15)—C(16)	1.382 (4)
C(8)—C(19)	1.514 (4)	C(18)—O(17)	1.429 (5)
C(8)—C(9)	1.543 (4)	C(19)—O(20)	1.234 (4)
C(8)—S(7)	1.804 (4)	C(19)—N(21)	1.337 (4)
C(9)—O(10)	1.418 (4)		
C(6)—C(1)—C(2)	120.9 (3)	C(16)—C(11)—C(12)	117.8 (3)
C(1)—C(2)—C(3)	118.6 (3)	C(16)—C(11)—C(9)	121.6 (3)
C(1)—C(2)—S(7)	121.7 (3)	C(12)—C(11)—C(9)	120.7 (3)
C(3)—C(2)—S(7)	119.7 (3)	C(13)—C(12)—C(11)	121.5 (3)
C(4)—C(3)—C(2)	119.9 (3)	C(14)—C(13)—C(12)	119.6 (3)
C(4)—C(3)—N(21)	119.4 (3)	C(15)—C(14)—O(17)	124.1 (3)
C(2)—C(3)—N(21)	120.7 (3)	C(15)—C(14)—C(13)	120.2 (3)
C(3)—C(4)—C(5)	120.9 (3)	O(17)—C(14)—C(13)	115.7 (3)
C(6)—C(5)—C(4)	119.5 (4)	C(14)—C(15)—C(16)	119.2 (3)
C(1)—C(6)—C(5)	120.2 (4)	C(11)—C(16)—C(15)	121.8 (3)
C(19)—C(8)—C(9)	113.0 (3)	O(20)—C(19)—N(21)	121.8 (3)
C(19)—C(8)—S(7)	110.2 (2)	O(20)—C(19)—C(8)	121.2 (3)
C(9)—C(8)—S(7)	111.8 (2)	N(21)—C(19)—C(8)	117.1 (3)
O(10)—C(9)—C(11)	112.1 (2)	C(19)—N(21)—C(3)	127.7 (3)
O(10)—C(9)—C(8)	105.5 (3)	C(14)—O(17)—C(18)	118.0 (3)
C(11)—C(9)—C(8)	110.8 (2)	C(2)—S(7)—C(8)	97.7 (2)
S(7)—C(2)—C(3)—N(21)	2.4 (4)		
S(7)—C(8)—C(9)—O(10)	172.1 (2)		
C(19)—C(8)—C(9)—C(11)	168.7 (3)		
C(9)—C(8)—C(19)—O(20)	-98.9 (4)		
S(7)—C(8)—C(19)—N(21)	-45.1 (4)		
C(8)—C(19)—N(21)—C(3)	4.5 (5)		
C(2)—C(3)—N(21)—C(19)	20.3 (5)		
C(3)—C(2)—S(7)—C(8)	-35.7 (3)		
C(19)—C(8)—S(7)—C(2)	54.7 (3)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N(21)—H(21)...O(20 ⁱ)	0.81 (3)	2.09 (3)	2.903 (3)	177 (3)
O(10)—H(10)...O(W)	0.85 (4)	1.93 (4)	2.763 (5)	169 (3)
O(W)—H(W1)...O(20 ⁱⁱ)	0.87 (6)	2.04 (5)	2.863 (5)	157 (5)

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

All non-H atoms were found by direct methods and the
parameters were refined successfully with a full-matrix least-
squares refinement procedure. H atoms were located on a
difference Fourier map and included in the refinement, the
refined H atoms having the bond lengths C—H 0.91–1.01 (5),
N—H 0.81 (3) and O—H 0.74–0.87 (4) \AA .

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(±)-*trans*-3-Hydroxy-2-(4-methoxy-phenyl)-4-oxo-2,3,4,5-tetrahydro-1,5-benzothiazepine 1-Oxide

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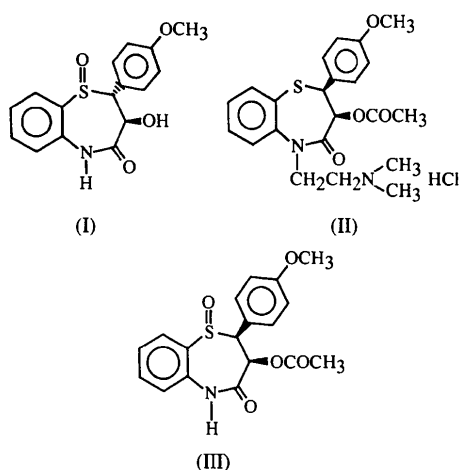
Abstract

The title compound, $\text{C}_{16}\text{H}_{15}\text{NO}_4\text{S}$, is a drug interme-
diate of diltiazem. The molecular packing is stabilized
by hydrogen bonding. The seven-membered ring is dis-

torted showing a twist-boat conformation. The benzene ring is planar, but the methoxyphenyl ring deviates significantly from planarity. The methoxyphenyl and hydroxy groups are *gauche* oriented with respect to one another. The methoxyphenyl group is axial and the carbonyl O atom is pseudo-axial to the seven-membered ring.

Comment

The title compound, (I), is one of the drug intermediates in the synthesis of diltiazem, (II). Diltiazem is an enantiomerically pure drug with calcium antagonist activity (Kojic-Prodic, Ruzic-Toros & Sunjic, 1984). Since the medicinal activity and structure of (I) is not yet known, an X-ray analysis was undertaken to study the conformation.



The structure of (I) (Fig. 1) is very similar to the diltiazem drug intermediate (III) (Kumaradhas & Nirmala, 1996) and has been compared with diltiazem, (II). Interatomic distances and angles in the seven-membered ring are similar to the seven-membered ring geometry of both (II) and (III). The bond lengths S(7)—C(2) [1.776 (4) Å] and C(9)—S(7) [1.835 (4) Å] are unequal as one is affected by the conjugation of the π -electron system. Bond lengths involving C_{sp³} atoms range from 1.508 (5) to 1.532 (5) Å. The carbonyl bonds fall into three categories: C_{sp³}—O single bonds [C(18)—O(19) 1.407 (5) and C(17)—O(16) 1.403 (7) Å], a C_{sp²}—O single bond [C(13)—O(16) 1.369 (6) Å] and a C=O double bond [C(20)—O(21) 1.230 (5) Å]. The C—N distances are unequal [C(3)—N(22) 1.421 (5) and C(20)—N(22) 1.332 (5) Å] due to different environments.

The conformation of the seven-membered ring was determined using the least-squares plane passing through atoms S(7), C(9) and C(18). Atoms C(2) and C(3) lie above, and atoms C(20) and N(22) lie below this plane. The values of the torsion angles of the seven-membered

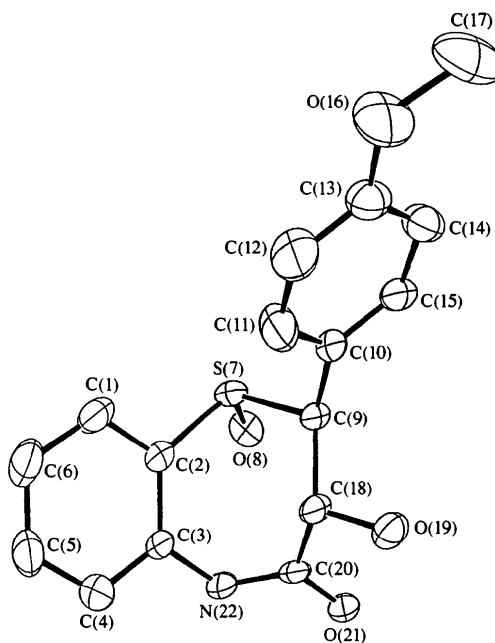


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

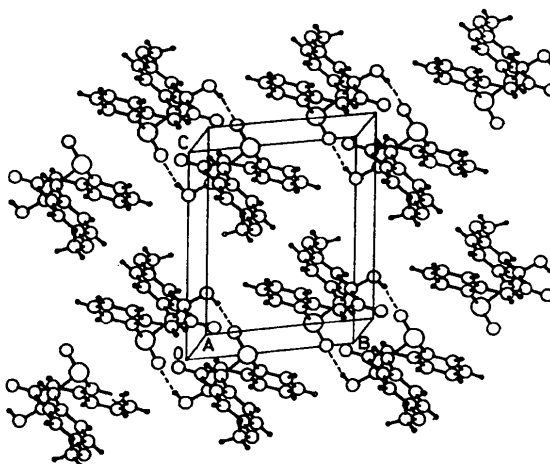


Fig. 2. Packing diagram of (I) viewed down the *a* axis. The O—H...O bonds are shown, but the N—H...O bonds, which are in the general direction of the *a* axis, are not.

ring show a twist-boat conformation (Hendrickson, 1961). The hydroxy and methoxyphenyl groups are attached to atoms C(18) and C(9), respectively, and are *gauche* oriented with respect to one another, as indicated by the C(10)—C(9)—C(18)—C(19) torsion angle of 61.5 (4)°. The dihedral angle between the seven-membered ring and the methoxyphenyl group is 72.4 (1)°. The methoxyphenyl group adopts an axial position in the molecule.

The packing arrangement in the unit cell is depicted in Fig. 2. The molecular packing is stabilized by hydro-

gen bonding (see Table 2). There are four intermolecular hydrogen bonds forming two dimers. One of the dimers (O—H...O) is shown in Fig. 2 and the other dimer (N—H...O) is in the projection of the *a* axis.

Experimental

The title compound was recrystallized from a mixture of ethanol and acetone at room temperature.

Crystal data

$C_{16}H_{15}NO_4S$

$M_r = 317.35$

Triclinic

$P\bar{1}$

$a = 7.721(4) \text{ \AA}$

$b = 8.695(2) \text{ \AA}$

$c = 11.347(9) \text{ \AA}$

$\alpha = 83.09(4)^\circ$

$\beta = 79.79(6)^\circ$

$\gamma = 81.38(2)^\circ$

$V = 737.8(7) \text{ \AA}^3$

$Z = 2$

$D_x = 1.429 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer

ω - 2θ scans

Absorption correction:

empirical via ψ scan

(North, Phillips &

Mathews, 1968)

$T_{\min} = 0.70$, $T_{\max} = 0.77$

2363 measured reflections

2175 independent reflections

Refinement

Refinement on F^2

$R(F) = 0.058$

$wR(F^2) = 0.140$

$S = 1.26$

2175 reflections

199 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 0.7749P]$

where $P = (F_o^2 + 2F_c^2)/3$

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 14 reflections

$\theta = 12$ – 23°

$\mu = 2.116 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Needle

$0.40 \times 0.20 \times 0.10 \text{ mm}$

Colourless

1726 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.0292$

$\theta_{\text{max}} = 60^\circ$

$h = 0 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -12 \rightarrow 12$

3 standard reflections

frequency: 60 min

intensity decay: $<2\%$

Table 1. Geometric parameters (\AA , $^\circ$)

C(1)—C(6)	1.378 (6)	C(10)—C(11)	1.383 (6)
C(1)—C(2)	1.395 (6)	C(11)—C(12)	1.371 (7)
C(2)—C(3)	1.393 (5)	C(12)—C(13)	1.377 (7)
C(2)—S(7)	1.776 (4)	C(13)—O(16)	1.369 (6)
C(3)—C(4)	1.379 (6)	C(13)—C(14)	1.372 (7)
C(3)—N(22)	1.421 (5)	C(14)—C(15)	1.385 (6)
C(4)—C(5)	1.381 (6)	C(17)—O(16)	1.403 (7)
C(5)—C(6)	1.380 (7)	C(18)—O(19)	1.407 (5)
C(9)—C(10)	1.508 (5)	C(18)—C(20)	1.531 (5)
C(9)—C(18)	1.532 (5)	C(20)—O(21)	1.230 (5)
C(9)—S(7)	1.835 (4)	C(20)—N(22)	1.332 (5)
C(10)—C(15)	1.368 (6)	O(8)—S(7)	1.503 (3)

C(6)—C(1)—C(2)	120.3 (4)	C(11)—C(12)—C(13)	119.7 (5)
C(3)—C(2)—C(1)	119.2 (4)	O(16)—C(13)—C(14)	124.6 (5)
C(3)—C(2)—S(7)	123.8 (3)	O(16)—C(13)—C(12)	115.0 (5)
C(1)—C(2)—S(7)	116.5 (3)	C(14)—C(13)—C(12)	120.4 (4)
C(4)—C(3)—C(2)	120.3 (4)	C(13)—C(14)—C(15)	118.7 (4)
C(4)—C(3)—N(22)	118.6 (3)	C(10)—C(15)—C(14)	122.0 (4)
C(2)—C(3)—N(22)	121.1 (3)	O(19)—C(18)—C(20)	108.6 (3)
C(3)—C(4)—C(5)	119.7 (4)	O(19)—C(18)—C(9)	110.0 (3)
C(6)—C(5)—C(4)	120.7 (4)	C(20)—C(18)—C(9)	113.1 (3)
C(1)—C(6)—C(5)	119.7 (4)	O(21)—C(20)—N(22)	122.9 (4)
C(10)—C(9)—C(18)	112.6 (3)	O(21)—C(20)—C(18)	119.4 (4)
C(10)—C(9)—S(7)	111.5 (3)	N(22)—C(20)—C(18)	117.6 (3)
C(18)—C(9)—S(7)	114.1 (3)	C(20)—N(22)—C(3)	125.7 (3)
C(15)—C(10)—C(11)	118.0 (4)	C(13)—O(16)—C(17)	118.2 (5)
C(15)—C(10)—C(9)	119.8 (4)	O(8)—S(7)—C(2)	107.1 (2)
C(11)—C(10)—C(9)	122.2 (4)	O(8)—S(7)—C(9)	106.0 (2)
C(12)—C(11)—C(10)	121.2 (4)	C(2)—S(7)—C(9)	100.4 (2)
S(7)—C(2)—C(3)—N(22)			−9.1 (6)
S(7)—C(9)—C(18)—C(20)			−48.3 (4)
C(9)—C(18)—C(20)—N(22)			83.1 (4)
C(18)—C(20)—N(22)—C(3)			−5.2 (6)
C(2)—C(3)—N(22)—C(20)			−46.3 (6)
C(3)—C(2)—S(7)—C(9)			67.9 (4)
C(18)—C(9)—S(7)—C(2)			−31.8 (3)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N(22)—H(22)...O(21 ⁱ)	0.860 (4)	2.049 (4)	2.854 (4)	155.4 (4)
O(19)—H(19)...O(8 ⁱⁱ)	0.82 (3)	2.04 (4)	2.831 (4)	162 (2)

Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $1 - x, -y, 2 - z$.

All non-H atoms were found by direct methods and their parameters were refined successfully with a full-matrix least-squares procedure. H atoms were geometrically positioned and refined using a riding model.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX* (Gabe, Le Page, White & Lee, 1987). Software used to prepare material for publication: *SHELXL93*.

The authors thank N. Kalyanam and SPIC Pharma for financial assistance and supplying the compound. We are also thankful to N. Karthikeyan, AIIMS and DST for the X-ray data collection.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1261). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

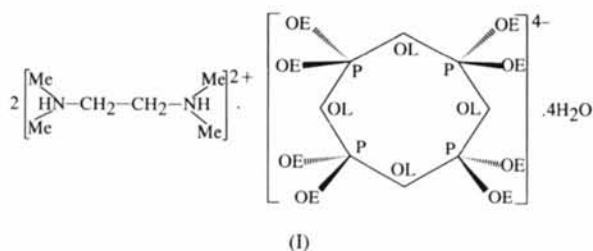
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Bis(*N,N,N',N'*-tetramethylethylenediammonium) Cyclotetraphosphate Tetrahydrate

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Abstract

The crystal structure of the title compound, 2C₆H₁₈N₂²⁺·P₄O₁₂⁴⁻·4H₂O, can be described as typical [(C₆H₁₈N₂)₂·P₄O₁₂]_n layers at $y = \frac{1}{2}$ interconnected by water molecules via hydrogen bonding.

Comment

The crystal structure of the title compound, (I), has been determined as part of an investigation into the solid-state chemistry of organic phosphates. Among the saturated organic amines RNH₂, R₂NH and R₃N, which are similar in their donor properties, only RNH₂ has been intensively studied with counterions HPO₄²⁻ (Averbuch-Pouchot & Durif, 1987), H₂PO₄⁻ (Kamoun, Jouini, Kamoun & Daoud, 1989), P₂O₇²⁻ (Kamoun, Jouini & Daoud, 1992), HP₂O₇³⁻ (Gharbi, Jouini, Averbuch-Pouchot & Durif, 1994), H₂P₂O₇²⁻ (Averbuch-Pouchot & Durif, 1993), P₃O₈³⁻ (Averbuch-Pouchot, Durif & Guitel, 1989), P₄O₁₂⁴⁻ (Jouini, 1989) and P₆O₁₈⁶⁻ (Durif & Averbuch-Pouchot, 1989). The alkylamine R₂NH has only been characterized three times, *i.e.* with monophosphate HPO₄²⁻ (Kamoun, Jouini & Daoud, 1990), cyclotetraphosphate P₄O₁₂⁴⁻ (Bdiri & Jouini, 1989) and cyclohexaphosphate P₆O₁₈⁶⁻ (Gharbi, Jouini & Durif, 1995). The first structure observed with alkylamine R₃N was *N,N,N',N'*-tetramethylethylenediammonium dihydrogendiphosphate dihydrate (Gharbi, Charfi & Jouini, 1996). The present work provides a second example of an R₃N compound comprising C₆H₁₈N₂²⁺ cations and P₄O₁₂⁴⁻ anions.

A projection of the atomic arrangement along the *b* axis is shown in Fig. 1. The two crystallographically independent organic C₆H₁₈N₂ entities and the P₄O₁₂ groups are located around the inversion centres at (0, $\frac{1}{2}$, 0), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and (0, $\frac{1}{2}$, $\frac{1}{2}$), respectively. The C₆H₁₈N₂²⁺ dication at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) is linked to P₄O₁₂⁴⁻ anions by hydrogen bonds, forming infinite anionic ribbons, [(C₆H₁₈N₂)₂·P₄O₁₂]_n²ⁿ⁻, along the *a* direction. The hydrogen bond involving the N2 atom of the remaining C₆H₁₈N₂ group at (0, $\frac{1}{2}$, 0) acts as a link between ribbons forming a two-dimensional [(C₆H₁₈N₂)₂·P₄O₁₂]_n network parallel to the *ac* plane. The N—H···O hydrogen bonds of this structure are strong since the corresponding N···O distances [2.647 (3) and 2.700 (3) Å] are of the same order of magnitude as the O···O distances inside the PO₄ tetrahedra. In addition, the H···O acceptor distances [1.81 (4) and 1.85 (4) Å] are shortest

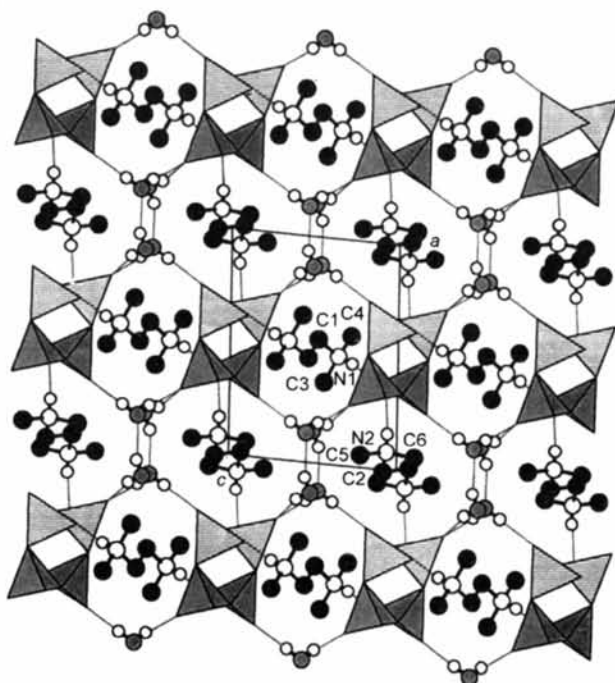


Fig. 1. Projection along the *b* direction of the structure of (I). P₄O₁₂ groups are in polyhedral representation, with large white circles representing N atoms, small circles H atoms, grey circles O atoms and black circles C atoms. Hydrogen bonds are denoted by full and dotted lines.