

N,N'-Dibenzylethane-1,2-diammonium dinitrate

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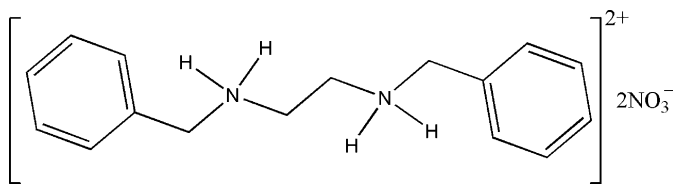
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.072; wR factor = 0.215; data-to-parameter ratio = 14.2.

The cation of the title compound, $\text{C}_{16}\text{H}_{22}\text{N}_2^{2+} \cdot 2\text{NO}_3^-$, resides on a crystallographic inversion centre (at the mid-point of the central C—C bond), with the nitrate anion on a general position. The ions are linked into chains by N—H...O hydrogen bonds and adjacent chains are further linked into sheets in the *ab* plane.

Related literature

For related literature, see: Allen *et al.* (1987); Bernstein *et al.* (1995); Liu *et al.* (2007); Xia *et al.* (2006, 2007).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{22}\text{N}_2^{2+} \cdot 2\text{NO}_3^-$
 $M_r = 366.38$
 Monoclinic, $P2_1/c$
 $a = 5.7889$ (15) Å
 $b = 5.5654$ (14) Å
 $c = 29.858$ (3) Å
 $\beta = 91.638$ (3)°

$V = 961.5$ (4) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 293$ (2) K
 $0.58 \times 0.23 \times 0.09$ mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.945$, $T_{\max} = 0.991$

4707 measured reflections
 1676 independent reflections
 942 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.215$
 $S = 1.02$
 1676 reflections

118 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O1 ⁱ	0.90	1.94	2.825 (3)	168
N1—H1A...O3 ⁱ	0.90	2.39	3.080 (3)	135
N1—H1B...O1	0.90	2.49	3.075 (3)	124
N1—H1B...O2	0.90	1.96	2.869 (3)	177
C1—H1C...O2 ⁱⁱ	0.97	2.58	3.204 (4)	123
C1—H1D...O3 ⁱⁱⁱ	0.97	2.53	3.377 (4)	147
C2—H2A...O3 ⁱⁱⁱ	0.97	2.49	3.367 (4)	150

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG3117).

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supplementary materials

Acta Cryst. (2007). E63, o3836 [doi:10.1107/S1600536807039736]

N,N'-Dibenzylethane-1,2-diammonium dinitrate

Y.-F. Liu, H.-T. Xia, D.-Q. Wang, S.-P. Yang and Y.-L. Meng

Comment

We have recently reported crystal structures of diamine derivatives, for example, *N,N'*-bis(2-hydroxy-3-methoxybenzyl) ethane-1,2-diamine (Xia *et al.*, 2006), *N,N'*-bis(2-hydroxy-3-methoxybenzyl) propane-1,2-diamine (Xia *et al.*, 2007). We have now continued our studied in this area with the title compound, (I). We compare the supramolecular aggregation in (I) with that in the analogous compound (II), a *o*-vanillin ethylenediamine nitrate (Liu *et al.*, 2007). In (II), the asymmetric unit consists of one cation, two half-cations and four anions in the space group $P\bar{1}$, and the cations are linked into two chains by C—H \cdots O hydrogen bonds: the nitrate anions linking two chains into a sheet parallel to the [001] plane.

In (I), the asymmetric unit consists of one half-cation and one anion. The cation has a inversion centre of at the mid-point of the central C—C bond (Fig. 1). The bond lengths and angles are normal (Allen *et al.*, 1987). The molecules are linked into a complex three-dimensional framework by a combination of N—H \cdots O, C—H \cdots O and C—H \cdots π hydrogen bonds (Table 2). However, the formation of the structure of (I) can be analysed in terms of two one-dimensional and one two-dimensional substructures.

In the first substructure, atoms N1 in the molecule at (x, y, z) and $(1 + x, y, z)$ act as hydrogen-bond donors to nitrate atoms O1, O2 and O3 in the molecule at (x, y, z) , respectively, and propagation by inversion and translation of these three hydrogen bonds generates a chain of rings parallel to the *a* axis direction, with $R_4^4(18)$ rings (Bernstein *et al.*, 1995) surrounds an $R_4^2(14)$ ring centred at $(n, 1, 0)$ ($n = \text{zero or integer}$) (Fig. 2).

In the second substructure, atoms C1 and C2 in the molecule at $(x, -1 + y, z)$ act as hydrogen-bond donors, respectively, to nitro atoms O2 in the molecule at (x, y, z) and O3 in the molecule at $(-1 + x, y, z)$, at the same time, atom N1 at (x, y, z) acts as a hydrogen-bond donor to nitro atom O1 in the molecule at $(-1 + x, y, z)$, so generating by a inversion centrosymmetric $R_4^4(20)$ motif centred at $(1/2, 1/2, 0)$. Propagation by inversion and translation of these three hydrogen bonds generates a chain parallel to the *b* axis direction containing $R_4^4(20)$ ring centred at $(1/2, 1/2 + n, 0)$ ($n = \text{zero or integer}$) (Fig. 3). The combination of the *a* and *b* chains generates a sheet running parallel to [001] plane.

The action of the two-dimensional substructure is to link adjacent cations into [100] sheets. Atom C6 in the molecule at (x, y, z) acts as a hydrogen-bond donor to *C*_g (aryl ring C3—C8) in the molecule at $(1 - x, -1/2 + y, 1/2 - z)$, so forming a sheet running parallel to the [100] plane, and generated by the 2_1 screw axis along $(1/2, y, 1/4)$ and by the *n*-glide plane at $y = 1/2$ (Fig. 4). The combination of the [001] and [100] sheets suffices to generate the three-dimensional framework structure. Hence it can be seen that the direction specific intermolecular interactions in compounds (I) and (II) are different, leading to markedly different supramolecular structures.

Experimental

To a solution of *N,N*-dibenzylethane-1,2-diamine (2 mmol) in methanol (20 ml) was added a solution of zinc(II) nitrate (1 mmol) in methanol (10 ml). The mixed solution was stirred for 4 h and then filtered. The solution was allowed to stand, slowly producing crystals of (I).

Refinement

The space group was uniquely assigned from the systematic absences. All H atoms were located in difference Fourier maps. H atoms bonded to C and N atoms were treated as riding atoms, with C—H distances of 0.93 Å (aryl), 0.97 Å (methylene), N—H distances of 0.90 Å (amine), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ (aryl, methylene, amine).

Figures

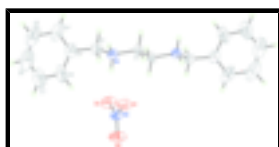


Fig. 1. The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are at the 30% probability level. Unlabelled atoms in the N1 cation are related to labelled atoms by $(1 - x, 2 - y, -z)$.



Fig. 2. A large part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain built from $\text{N—H}\cdots\text{O}$. For clarity, H atoms not involved in the hydrogen bonding have been omitted. Dashed lines indicate hydrogen bonds: [symmetry code: (A) $1 + x, y, z$].

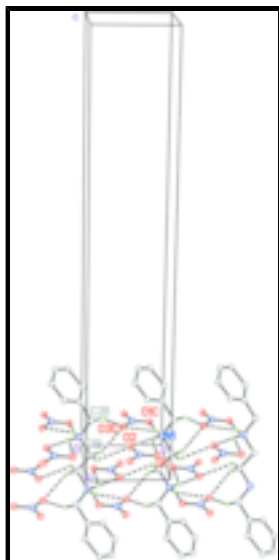


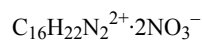
Fig. 3. A large part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain built from N—H...O and C—H...O. For clarity, H atoms not involved in the hydrogen bonding have been omitted. Dashed lines indicate hydrogen bonds. [symmetry code: (B) $x, -1 + y, z$, (C) $-1 + x, y, z$].



Fig. 4. The crystal structure of (I). Neighboring chains are connected by C—H... π hydrogen bonds. For clarity, H atoms not involved in the hydrogen bonding have been omitted. Dashed lines indicate hydrogen bonds. [symmetry code: (D) $1 - x, -1/2 + y, 1/2 - z$].

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Crystal data



$M_r = 366.38$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 5.7889$ (15) Å

$b = 5.5654$ (14) Å

$c = 29.858$ (3) Å

$\beta = 91.638$ (3)°

$V = 961.5$ (4) Å³

$Z = 2$

$F_{000} = 388$

$D_x = 1.265$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 995 reflections

$\theta = 2.7\text{--}22.8^\circ$

$\mu = 0.10$ mm⁻¹

$T = 293$ (2) K

Block, colourless

$0.58 \times 0.23 \times 0.09$ mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.945$, $T_{\max} = 0.991$

1676 independent reflections

942 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 1.4^\circ$

$h = -6 \rightarrow 6$

$k = -6 \rightarrow 6$

supplementary materials

4707 measured reflections

$l = -31 \rightarrow 35$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.072$

H-atom parameters constrained

$wR(F^2) = 0.215$

$$w = 1/[\sigma^2(F_o^2) + (0.1189P)^2]$$

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

$S = 1.02$

$(\Delta/\sigma)_{\max} < 0.001$

1676 reflections

$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$

118 parameters

$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.4744 (4)	0.9458 (4)	0.06168 (7)	0.0488 (7)
H1A	0.3281	0.8909	0.0607	0.059*
H1B	0.5690	0.8174	0.0626	0.059*
N2	0.9771 (5)	0.6263 (5)	0.05954 (9)	0.0599 (8)
O1	0.9957 (4)	0.8469 (4)	0.05704 (9)	0.0742 (8)
O2	0.7799 (5)	0.5400 (4)	0.06156 (10)	0.0882 (9)
O3	1.1532 (5)	0.5046 (4)	0.05864 (12)	0.1054 (11)
C1	0.5158 (5)	1.0821 (5)	0.01998 (9)	0.0478 (8)
H1C	0.6714	1.1468	0.0209	0.057*
H1D	0.4081	1.2154	0.0174	0.057*
C2	0.5114 (6)	1.0864 (5)	0.10331 (11)	0.0617 (9)
H2A	0.4219	1.2336	0.1014	0.074*
H2B	0.6733	1.1295	0.1066	0.074*
C3	0.4409 (7)	0.9453 (7)	0.14330 (12)	0.0719 (10)
C4	0.2417 (10)	0.9825 (12)	0.16382 (17)	0.132 (2)
H4	0.1406	1.1026	0.1540	0.158*
C5	0.1848 (15)	0.827 (2)	0.2029 (2)	0.161 (3)

H5	0.0499	0.8447	0.2187	0.194*
C6	0.347 (2)	0.656 (2)	0.2133 (3)	0.159 (3)
H6	0.3149	0.5565	0.2374	0.191*
C7	0.5403 (19)	0.6153 (13)	0.1939 (2)	0.152 (3)
H7	0.6420	0.4952	0.2034	0.182*
C8	0.5840 (11)	0.7599 (9)	0.15861 (14)	0.1118 (17)
H8	0.7199	0.7332	0.1435	0.134*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0431 (14)	0.0402 (12)	0.0633 (16)	-0.0065 (10)	0.0058 (11)	0.0016 (12)
N2	0.0537 (18)	0.0480 (16)	0.0781 (19)	-0.0011 (14)	0.0037 (13)	-0.0052 (14)
O1	0.0509 (15)	0.0458 (13)	0.126 (2)	-0.0046 (10)	0.0056 (13)	0.0070 (13)
O2	0.0651 (17)	0.0567 (14)	0.143 (2)	-0.0189 (13)	0.0094 (15)	0.0008 (15)
O3	0.0756 (19)	0.0674 (16)	0.174 (3)	0.0276 (14)	0.0076 (18)	-0.0031 (17)
C1	0.0504 (17)	0.0350 (14)	0.0584 (18)	-0.0032 (13)	0.0059 (14)	0.0043 (13)
C2	0.075 (2)	0.0476 (17)	0.063 (2)	-0.0073 (16)	0.0040 (16)	-0.0075 (16)
C3	0.074 (3)	0.082 (3)	0.060 (2)	-0.023 (2)	0.0055 (19)	-0.009 (2)
C4	0.109 (4)	0.205 (6)	0.082 (3)	-0.028 (4)	0.033 (3)	-0.033 (4)
C5	0.123 (6)	0.261 (10)	0.102 (5)	-0.062 (6)	0.040 (4)	-0.034 (6)
C6	0.177 (8)	0.191 (8)	0.112 (5)	-0.077 (7)	0.036 (6)	-0.005 (5)
C7	0.238 (9)	0.132 (5)	0.085 (4)	-0.005 (6)	0.004 (5)	0.021 (4)
C8	0.176 (5)	0.095 (3)	0.064 (3)	-0.009 (3)	0.003 (3)	0.015 (3)

Geometric parameters (\AA , $^\circ$)

N1—C2	1.479 (4)	C2—H2B	0.9700
N1—C1	1.484 (3)	C3—C4	1.337 (6)
N1—H1A	0.9000	C3—C8	1.392 (6)
N1—H1B	0.9000	C4—C5	1.498 (10)
N2—O3	1.225 (3)	C4—H4	0.9300
N2—O1	1.235 (3)	C5—C6	1.367 (11)
N2—O2	1.241 (3)	C5—H5	0.9300
C1—C1 ⁱ	1.510 (6)	C6—C7	1.294 (11)
C1—H1C	0.9700	C6—H6	0.9300
C1—H1D	0.9700	C7—C8	1.355 (8)
C2—C3	1.496 (5)	C7—H7	0.9300
C2—H2A	0.9700	C8—H8	0.9300
C2—N1—C1	114.3 (2)	H2A—C2—H2B	108.0
C2—N1—H1A	108.7	C4—C3—C8	118.5 (5)
C1—N1—H1A	108.7	C4—C3—C2	122.9 (5)
C2—N1—H1B	108.7	C8—C3—C2	118.6 (4)
C1—N1—H1B	108.7	C3—C4—C5	118.6 (7)
H1A—N1—H1B	107.6	C3—C4—H4	120.7
O3—N2—O1	118.4 (3)	C5—C4—H4	120.7
O3—N2—O2	123.6 (3)	C6—C5—C4	114.5 (7)
O1—N2—O2	118.0 (3)	C6—C5—H5	122.7

supplementary materials

N1—C1—C1 ⁱ	109.5 (3)	C4—C5—H5	122.7
N1—C1—H1C	109.8	C7—C6—C5	128.0 (8)
C1 ⁱ —C1—H1C	109.8	C7—C6—H6	116.0
N1—C1—H1D	109.8	C5—C6—H6	116.0
C1 ⁱ —C1—H1D	109.8	C6—C7—C8	115.4 (8)
H1C—C1—H1D	108.2	C6—C7—H7	122.3
N1—C2—C3	110.9 (2)	C8—C7—H7	122.3
N1—C2—H2A	109.5	C7—C8—C3	124.9 (6)
C3—C2—H2A	109.5	C7—C8—H8	117.5
N1—C2—H2B	109.5	C3—C8—H8	117.5
C3—C2—H2B	109.5		
C2—N1—C1—C1 ⁱ	177.3 (3)	C3—C4—C5—C6	-0.7 (9)
C1—N1—C2—C3	173.6 (3)	C4—C5—C6—C7	0.3 (12)
N1—C2—C3—C4	-102.3 (4)	C5—C6—C7—C8	-0.6 (12)
N1—C2—C3—C8	74.7 (4)	C6—C7—C8—C3	1.3 (9)
C8—C3—C4—C5	1.4 (7)	C4—C3—C8—C7	-1.8 (7)
C2—C3—C4—C5	178.4 (4)	C2—C3—C8—C7	-178.9 (5)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O1 ⁱⁱ	0.90	1.94	2.825 (3)	168
N1—H1A \cdots O3 ⁱⁱ	0.90	2.39	3.080 (3)	135
N1—H1B \cdots O1	0.90	2.49	3.075 (3)	124
N1—H1B \cdots O2	0.90	1.96	2.869 (3)	177
C1—H1C \cdots O2 ⁱⁱⁱ	0.97	2.58	3.204 (4)	123
C1—H1D \cdots O3 ^{iv}	0.97	2.53	3.377 (4)	147
C2—H2A \cdots O3 ^{iv}	0.97	2.49	3.367 (4)	150

Symmetry codes: (ii) $x-1, y, z$; (iii) $x, y+1, z$; (iv) $x-1, y+1, z$.

Fig. 1

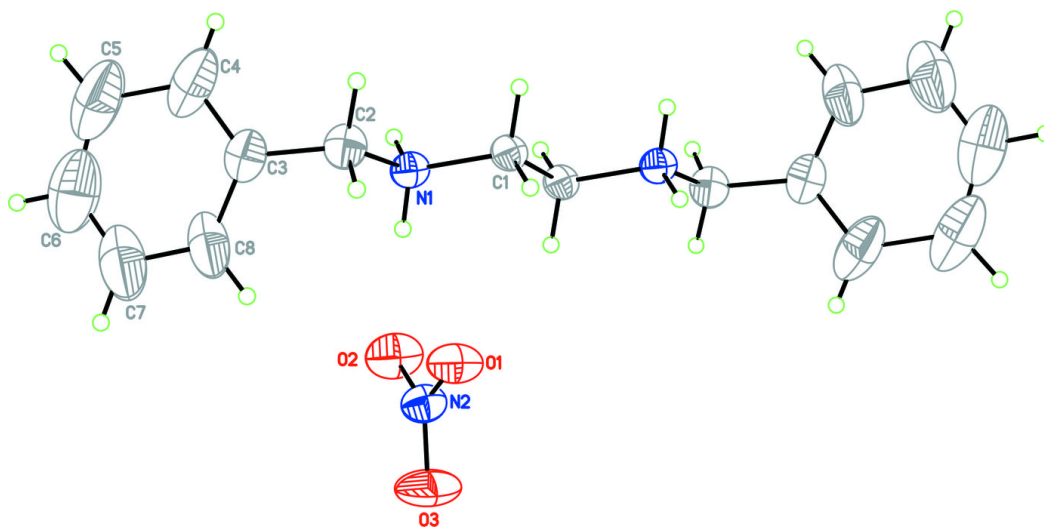


Fig. 2

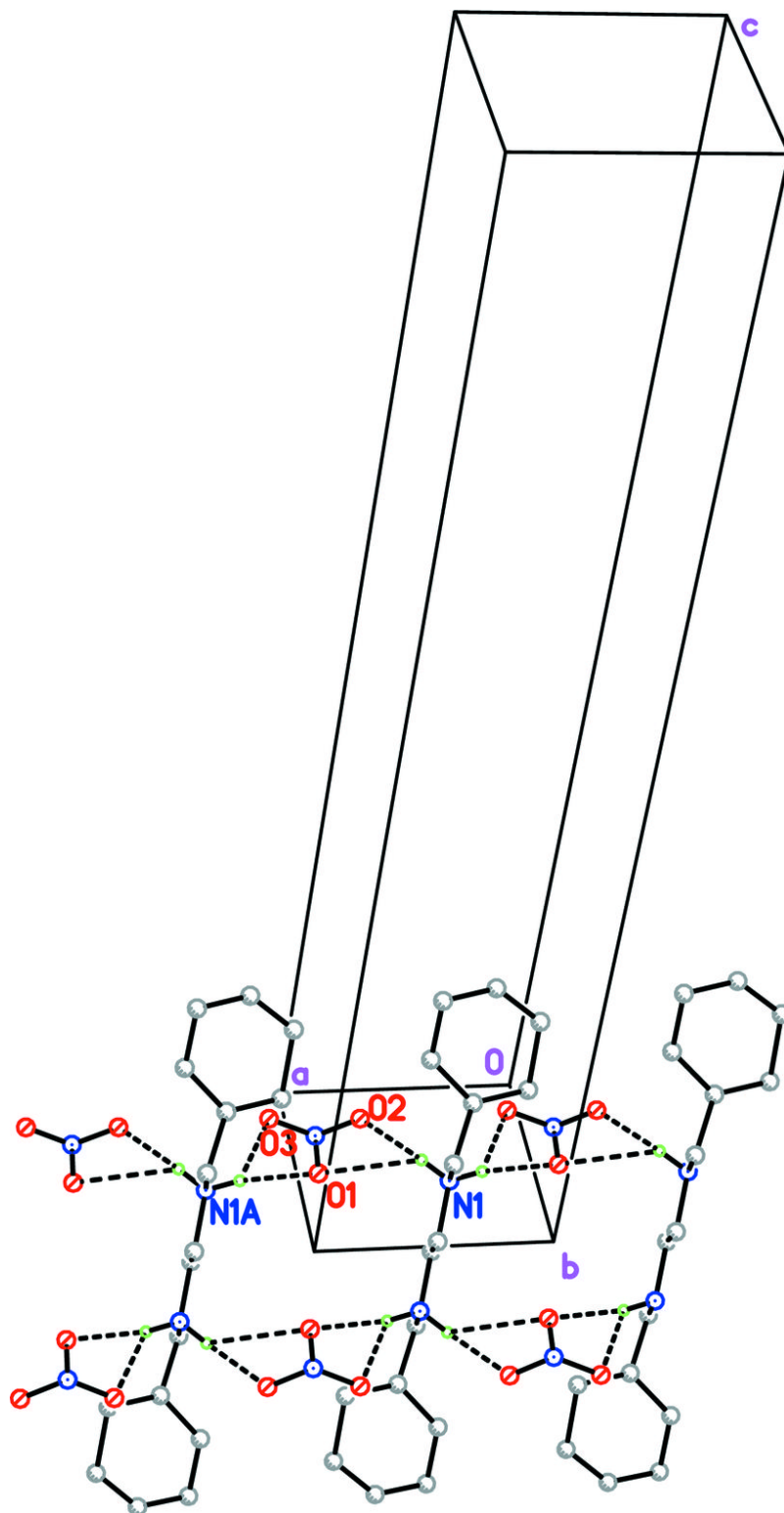


Fig. 3

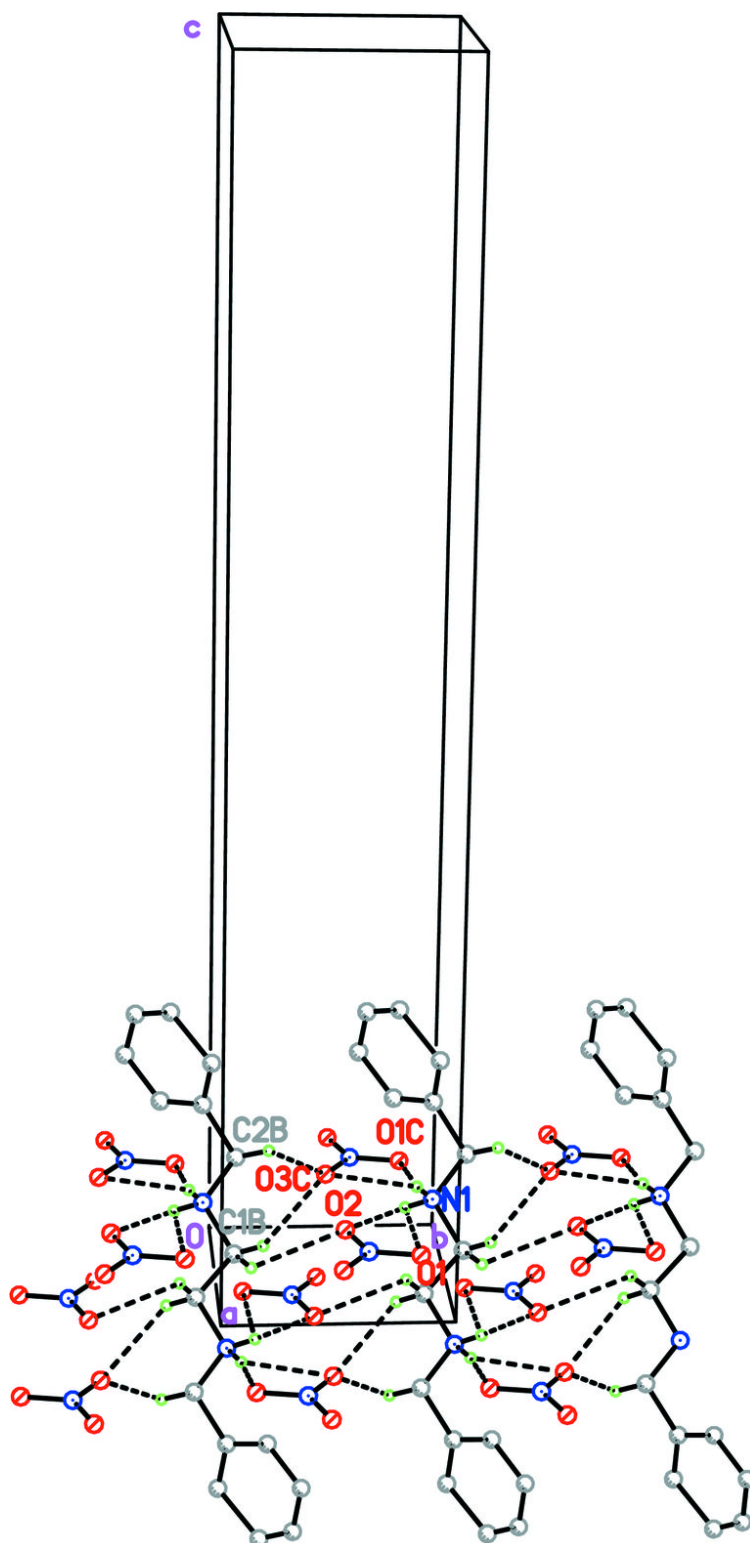


Fig. 4

