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4-Methoxybenzylammonium nitrate

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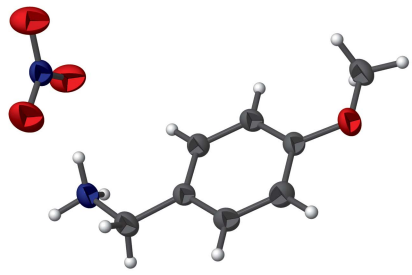
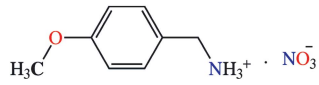
Structural data: full structural data are available from iucrdata.iucr.org

In the title salt, $C_8H_{12}NO^+\cdot NO_3^-$, the 4-methoxybenzylammonium cation lies in the mirror plane *m* of space group *Pnma* and is thus planar by symmetry. The nitrate anion is also planar by symmetry, with an N···O group in the mirror plane and one O atom in a general position. The dihedral angle between the benzene ring and the planar nitrate anion is constrained to be exactly 90°, because of the relative special positions for both ions. In the crystal, the cations are connected to the anions by C—H···O, C—H···N, N—H···N and N—H···O hydrogen bonds. Further, the crystal structure also features two C—H···π interactions involving the benzene ring of the cation, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

Single crystals play an important role in non-linear optics. Non-linear optical materials have been of great interest among researchers in various applications such as laser frequency conversion, optical communication and optical data storage over the past few decades (Liu *et al.*, 2015). Organic crystals possess greater non-linear susceptibility and fast response time, while inorganic crystals exhibit high mechanical and thermal properties (Vigneshwaran *et al.*, 2017). Semi-organic crystals are expected to have the combined advantages of both organic and inorganic crystals. 4-Methoxybenzylamine based derivatives exhibit second order non-linear optical properties (Mahbouli Rhouma *et al.*, 2016). These materials also possess antimicrobial activity (Joshi *et al.*, 2014).

In the title salt, $C_8H_{12}NO^+\cdot NO_3^-$ (Fig. 1), the 4-methoxybenzylammonium cation lies in the mirror *m* plane of space group *Pnma* (with some exceptions for H atoms bonded to tetrahedral sites: H1*B*, H1*D* and H8, which are in general positions). The cation is thus planar by symmetry. The nitrate anion is also planar, with atoms N2 and O3 placed in the mirror plane *m*. The dihedral angle between the benzene ring and the planar nitrate group is constrained to be exactly 90° by symmetry.

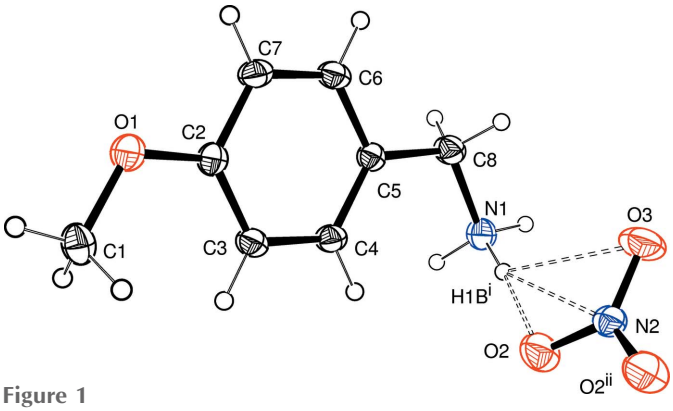


Figure 1
An *ORTEP* view of the title salt, with displacement ellipsoids drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines. [Symmetry codes: (i) $x, \frac{1}{2}-y, z$; (ii) $x, \frac{3}{2}-y, z$.]

In the crystal, analysis of potential hydrogen bonds shows that the cations are connected to the nitrate anions by C7—H7···O3, C1—H1*C*···N2, N1—H1*A*···N2, N1—H1*A*···O2, N1—H1*A*···O2, N1—H1*B*···N2, and N1—H1*B*···O2 hydrogen bonds (Fig. 2 and Table 1). Further, the crystal structure features two C1—H1*D*···π interactions involving the benzene (C2–C7) ring, leading to the formation of a three-dimensional network (Table 1).

The crystal structure of 4-methylbenzylammonium nitrate, closely related to the title compound, has been reported in space group $P2_1/c$ (Gatfaoui *et al.*, 2013): in that case, both the cation and anion are placed in general positions, and the N atom of the 4-methylbenzylammonium cation is displaced by 1.366 (2) Å from the mean plane of the other atoms.

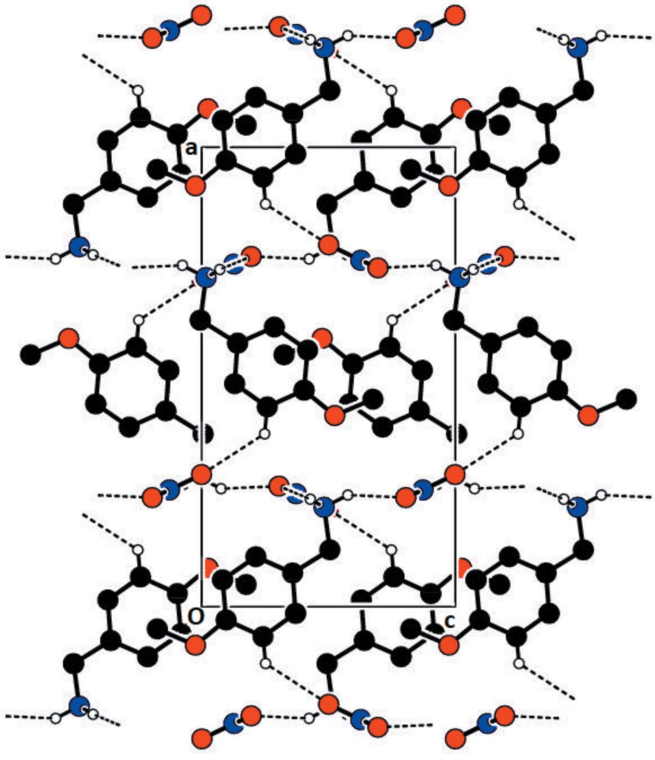


Figure 2
The crystal structure of the title salt, viewed along the *b* axis, showing the formation of hydrogen bonding. Dashed lines indicate hydrogen bonds and H atoms not involved in hydrogen bonds have been omitted.

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C2–C7 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O3^{i}	0.93	2.59	3.249 (2)	128
C1—H1*C*···N2^{ii}	0.98 (3)	2.61 (3)	3.568 (3)	166 (3)
N1—H1*A*···N2^{iii}	0.92 (3)	2.59 (3)	3.452 (2)	157 (2)
N1—H1*A*···O2^{iii}	0.92 (3)	2.26 (3)	3.022 (2)	140 (2)
N1—H1*A*···O2^{iv}	0.92 (3)	2.26 (3)	3.022 (2)	140 (2)
N1—H1*B*···N2^{v}	0.96 (2)	2.67 (2)	3.5717 (8)	156.4 (18)
N1—H1*B*···O2^{vi}	0.96 (2)	1.94 (2)	2.9039 (16)	175.0 (19)
C1—H1*D*···*Cg*1^{vii}	0.978 (19)	2.65 (2)	3.4625 (5)	141.4 (14)
C1—H1*D*···*Cg*1^{viii}	0.978 (19)	2.65 (2)	3.4625 (5)	141.4 (14)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+\frac{3}{2}, -y+1, z-\frac{1}{2}$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (v) $x, y-1, z$; (vi) $x, -y+\frac{1}{2}, z$; (vii) $x+\frac{3}{2}, -y-\frac{1}{2}, -z+\frac{2}{2}$; (viii) $-x+1, -y, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{12}NO^+\cdot NO_3^-$
M_r	200.20
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	296
a, *b*, *c* (Å)	15.8203 (17), 6.8156 (7), 8.7275 (8)
V (Å^3)	941.04 (16)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.11
Crystal size (mm)	0.25 × 0.20 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.696, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18099, 1663, 1126
R_{int}	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.740
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.040, 0.131, 1.06
No. of reflections	1663
No. of parameters	101
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.19

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1993), *SHELXL2017* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2015) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

4-Methoxybenzylammonium nitrate crystals were synthesized by mixing 4-methoxybenzylamine (2 mmol, 0.274 g), dilute nitric acid (2 ml, 1 mol) and nickel nitrate (1 mmol, 0.291 g) in doubly distilled water. This solution was stirred continuously for about 3 h using a magnetic stirrer and then allowed to evaporate slowly at room temperature. Colourless crystals of

the title compound suitable for single-crystal X-ray analysis were obtained after two weeks.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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4-Methoxybenzylammonium nitrate

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4-Methoxybenzylammonium nitrate

Crystal data

$C_8H_{12}NO^+·NO_3^-$
M_r = 200.20
Orthorhombic, *Pnma*
a = 15.8203 (17) Å
b = 6.8156 (7) Å
c = 8.7275 (8) Å
V = 941.04 (16) Å^3
Z = 4
F(000) = 424
D_x = 1.413 Mg m^{-3}
Melting point: 375 K
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 4546 reflections
θ = 2.6–29.6°
μ = 0.11 mm^{-1}
T = 296 K
Block, colourless
0.25 × 0.20 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.696, T_{max} = 0.746
18099 measured reflections
1663 independent reflections
1126 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 31.7°, θ_{min} = 2.6°
h = −23→23
k = −9→9
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.131
S = 1.06
1663 reflections
101 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.2894P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: SHELXL2017 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.021 (3)

Special details

Refinement. The N-bound H atoms, CH_2 H atoms and CH_3 H atoms were located in a difference Fourier map and refined freely; N1—H1A = 0.92 (3) and N1—H1B = 0.96 (2) Å, C8—H8 = 0.971 (18), C1—H1C = 0.98 (3) and C1—H1D = 0.978 (19) Å. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å (aromatic); U_{iso}(H) = 1.2U_{eq}(C).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.45170 (15)	0.250000	0.6753 (2)	0.0419 (5)
C2	0.47135 (11)	0.250000	0.4038 (2)	0.0305 (4)
C3	0.55852 (11)	0.250000	0.4177 (2)	0.0341 (4)
H3	0.583441	0.250000	0.514185	0.041*
C4	0.60883 (11)	0.250000	0.2864 (2)	0.0334 (4)
H4	0.667343	0.250000	0.296668	0.040*
C5	0.57361 (11)	0.250000	0.14141 (19)	0.0291 (4)
C6	0.48549 (11)	0.250000	0.1299 (2)	0.0353 (4)
H6	0.460461	0.250000	0.033433	0.042*
C7	0.43498 (11)	0.250000	0.2584 (2)	0.0373 (4)
H7	0.376470	0.250000	0.248118	0.045*
C8	0.62382 (12)	0.250000	−0.0055 (2)	0.0388 (4)
N1	0.71654 (11)	0.250000	0.0170 (2)	0.0377 (4)
N2	0.74586 (10)	0.750000	0.12747 (17)	0.0354 (4)
O1	0.41614 (8)	0.250000	0.52492 (15)	0.0414 (4)
O2	0.76246 (8)	0.59369 (17)	0.19519 (14)	0.0569 (4)
O3	0.71238 (11)	0.750000	0.00086 (18)	0.0616 (5)
H1A	0.7431 (17)	0.250000	−0.076 (4)	0.059 (7)*
H1B	0.7340 (13)	0.134 (3)	0.071 (3)	0.077 (6)*
H1C	0.404 (2)	0.250000	0.747 (4)	0.077 (9)*
H1D	0.4873 (11)	0.135 (3)	0.692 (2)	0.058 (5)*
H8	0.6126 (11)	0.135 (3)	−0.067 (2)	0.061 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0487 (12)	0.0453 (12)	0.0317 (9)	0.000	0.0074 (8)	0.000
C2	0.0310 (8)	0.0295 (8)	0.0312 (8)	0.000	0.0025 (6)	0.000
C3	0.0326 (9)	0.0433 (10)	0.0264 (8)	0.000	−0.0036 (7)	0.000
C4	0.0255 (8)	0.0442 (10)	0.0306 (8)	0.000	−0.0017 (6)	0.000
C5	0.0291 (8)	0.0301 (8)	0.0280 (8)	0.000	−0.0007 (6)	0.000
C6	0.0338 (9)	0.0435 (10)	0.0287 (8)	0.000	−0.0067 (7)	0.000
C7	0.0257 (8)	0.0485 (11)	0.0377 (9)	0.000	−0.0045 (7)	0.000
C8	0.0352 (9)	0.0529 (13)	0.0284 (8)	0.000	−0.0003 (7)	0.000
N1	0.0357 (8)	0.0455 (10)	0.0319 (8)	0.000	0.0053 (6)	0.000
N2	0.0278 (7)	0.0464 (9)	0.0319 (7)	0.000	0.0016 (6)	0.000
O1	0.0337 (7)	0.0559 (9)	0.0347 (7)	0.000	0.0057 (5)	0.000
O2	0.0783 (8)	0.0383 (6)	0.0541 (7)	−0.0045 (5)	−0.0173 (6)	0.0043 (5)
O3	0.0567 (10)	0.0924 (14)	0.0357 (8)	0.000	−0.0140 (7)	0.000

Geometric parameters (Å, º)

C1—O1	1.428 (2)	C5—C8	1.508 (2)
C1—H1C	0.98 (3)	C6—C7	1.377 (3)
C1—H1D	0.978 (19)	C6—H6	0.9300

C1—H1D^{i}	0.978 (19)	C7—H7	0.9300
C2—O1	1.371 (2)	C8—N1	1.480 (3)
C2—C3	1.384 (2)	C8—H8	0.971 (18)
C2—C7	1.393 (2)	C8—H8^{i}	0.971 (18)
C3—C4	1.395 (2)	N1—H1A	0.92 (3)
C3—H3	0.9300	N1—H1B	0.96 (2)
C4—C5	1.383 (2)	N2—O3	1.225 (2)
C4—H4	0.9300	N2—O2^{ii}	1.2463 (14)
C5—C6	1.398 (2)	N2—O2	1.2463 (14)
O1—C1—H1C	106.1 (18)	C7—C6—H6	119.3
O1—C1—H1D	111.3 (11)	C5—C6—H6	119.3
H1C—C1—H1D	110.5 (14)	C6—C7—C2	120.15 (16)
O1—C1—H1D^{i}	111.3 (11)	C6—C7—H7	119.9
H1C—C1—H1D^{i}	110.5 (14)	C2—C7—H7	119.9
H1D—C1—H1D^{i}	107 (2)	N1—C8—C5	114.15 (15)
O1—C2—C3	124.53 (15)	N1—C8—H8	104.8 (10)
O1—C2—C7	116.05 (15)	C5—C8—H8	112.1 (11)
C3—C2—C7	119.43 (16)	N1—C8—H8^{i}	104.8 (10)
C2—C3—C4	119.76 (16)	C5—C8—H8^{i}	112.1 (11)
C2—C3—H3	120.1	H8—C8—H8^{i}	108 (2)
C4—C3—H3	120.1	C8—N1—H1A	109.6 (17)
C5—C4—C3	121.44 (15)	C8—N1—H1B	110.5 (12)
C5—C4—H4	119.3	H1A—N1—H1B	107.8 (15)
C3—C4—H4	119.3	O3—N2—O2^{ii}	121.25 (8)
C4—C5—C6	117.90 (15)	O3—N2—O2	121.25 (8)
C4—C5—C8	124.46 (15)	O2^{ii}—N2—O2	117.48 (16)
C6—C5—C8	117.64 (15)	C2—O1—C1	117.24 (14)
C7—C6—C5	121.32 (16)		
O1—C2—C3—C4	180.000 (1)	C5—C6—C7—C2	0.000 (1)
C7—C2—C3—C4	0.000 (1)	O1—C2—C7—C6	180.000 (1)
C2—C3—C4—C5	0.000 (1)	C3—C2—C7—C6	0.000 (1)
C3—C4—C5—C6	0.000 (1)	C4—C5—C8—N1	0.0
C3—C4—C5—C8	180.000 (1)	C6—C5—C8—N1	180.0
C4—C5—C6—C7	0.000 (1)	C3—C2—O1—C1	0.000 (1)
C8—C5—C6—C7	180.000 (1)	C7—C2—O1—C1	180.000 (1)

Symmetry codes: (i) x, $-y+1/2$, z; (ii) x, $-y+3/2$, z.

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C2–C7 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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N1—H1*B*···O2^{i}	0.96 (2)	1.94 (2)	2.9039 (16)	175.0 (19)
C1—H1*D*···*Cg*1^{viii}	0.978 (19)	2.65 (2)	3.4625 (5)	141.4 (14)
C1—H1*D*···*Cg*1^{ix}	0.978 (19)	2.65 (2)	3.4625 (5)	141.4 (14)

Symmetry codes: (i) *x*, −*y*+1/2, *z*; (iii) −*x*+1, −*y*+1, −*z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+3/2, −*y*+1, *z*−1/2; (vi) −*x*+3/2, *y*−1/2, *z*−1/2; (vii) *x*, *y*−1, *z*; (viii) *x*+3/2, −*y*−1/2, −*z*+3/2; (ix) −*x*+1, −*y*, −*z*+1.