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2-Amino-3-methylpyridinium 4-methoxybenzoate

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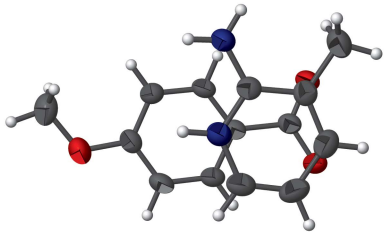
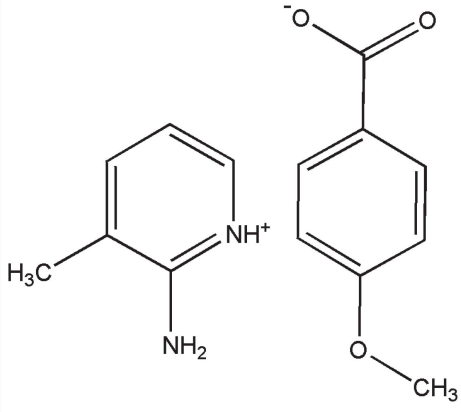
In the title molecular salt, $C_6H_9N_2^+\cdot C_8H_7O_3^-$, the cation is protonated at its pyridine N atom and is inclined by 3.39 (9)° to the benzene ring of the anion, which is deprotonated at the carboxyl group. The methoxy group is twisted with respect to the benzene ring to which it is attached, the methyl C atom deviating from the ring plane by 0.023 (2) Å. In the crystal, the anions and cations are linked by two N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif. They are also linked by a weak offset π–π interaction [centroid-to-centroid distance = 3.890 (1) Å]. The anions and cations are further connected through N—H···O and C—H···O hydrogen bonds, forming slabs parallel to (001).

3D view



Chemical scheme



Structure description

Pyridine derivatives have been shown to exhibit anticancer (Girgis *et al.* 2006) and antiviral (Hamdouchi *et al.*, 1999) activities. As part of our studies in this area we synthesized the title compound and report herein on its synthesis and crystal structure.

The geometric parameters of the title compound, Fig. 1, are comparable with those reported for similar structures (Babu *et al.*, 2014; Sivakumar *et al.*, 2016). The asymmetric unit contains a 2-amino-3-methylpyridinium cation, which is protonated at the pyridine N atom and a 4-methoxybenzoate anion which is deprotonated at the carboxyl group. They are linked by two N—H···O hydrogen bonds, forming $R_2^2(8)$ ring-motifs (Table 1 and Fig. 2). They are also linked by a weak offset π–π interaction [$Cg1\cdots Cg2$ = 3.890 (1) Å, interplanar distance = 3.487 (1) Å, slippage = 1.896 Å, $Cg1$ and $Cg2$ are the centroids of rings C1–C6 and N1/C9–C13, respectively]. The benzene ring (C1–C6) makes a dihedral angle of 3.39 (9)° with the pyridine ring (N1/C9–C13). The methoxy group is twisted with respect to the benzene ring, the methyl atom C17 deviating from the ring plane by 0.023 (2) Å. The mean plane of the methoxy group (C1/O1/C7) is twisted at an angle of 3.49 (17)° with respect to the attached benzene ring.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.89 (1)	1.69 (1)	2.573 (2)	174 (2)
N2—H2A···O3^{i}	0.86	2.01	2.8680 (19)	175
N2—H2B···O3^{ii}	0.86	2.12	2.924 (2)	155
C2—H2···O2^{iii}	0.93	2.57	3.419 (2)	152
C10—H10···O1^{iv}	0.93	2.59	3.356 (2)	140

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+\frac{5}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

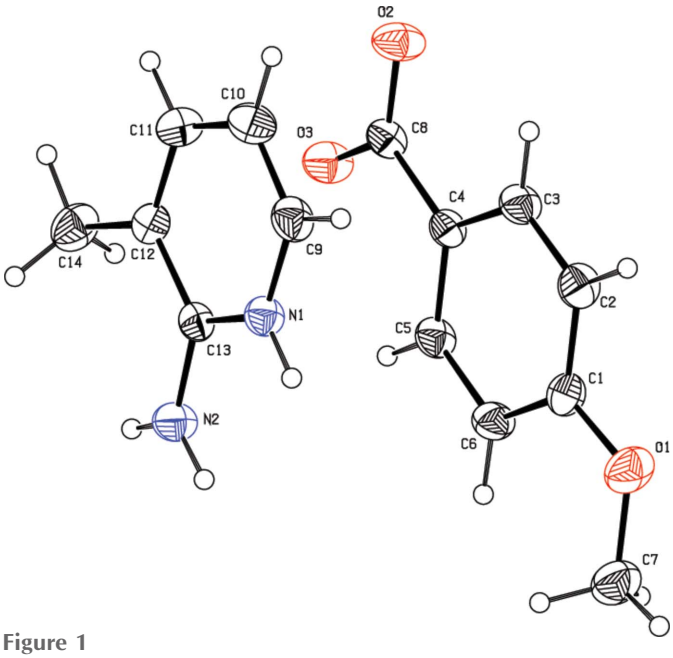


Figure 1
The molecular structure of the title molecular salt, showing the atom labelling and 30% probability displacement ellipsoids.

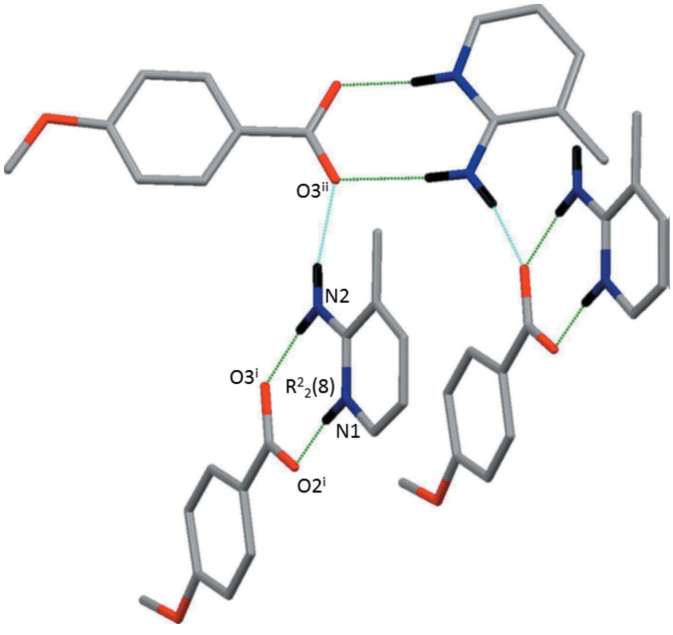


Figure 2
A partial view of the crystal packing of the title molecular salt, showing the $R_2^2(8)$ ring motifs. The hydrogen bonds are shown as dashed lines (see Table 1 for details).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_9N_2^+\cdot C_8H_7O_3^-$
M_r	260.29
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	295
a, b, c (Å)	12.2526 (8), 6.6872 (3), 16.6376 (12)
β (°)	103.836 (4)
V (Å^3)	1323.66 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.26 × 0.24 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.976, 0.982
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18167, 3737, 2223
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.697
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.151, 1.08
No. of reflections	3737
No. of parameters	178
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008).

In the crystal, the anions and cations are further connected through N—H···O and C—H···O hydrogen bonds, forming slabs parallel to the *ab* plane (Table 1 and Fig. 3).

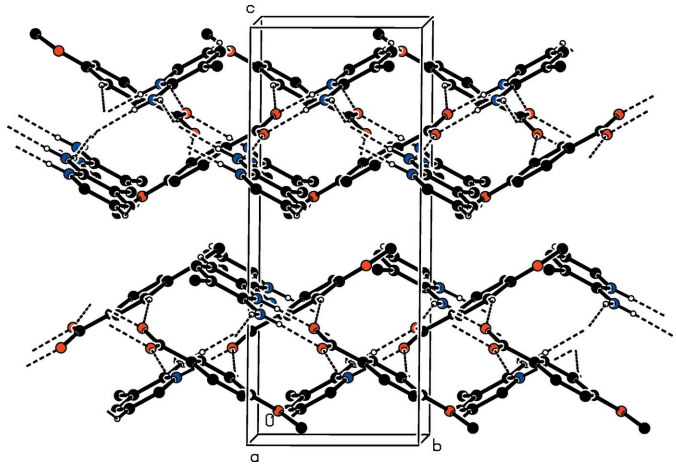


Figure 3
The crystal packing of the title compound viewed along the *a* axis. The hydrogen bonds are shown as dashed lines. C-bound H atoms which are not involved in these interactions have been omitted for clarity.

Synthesis and crystallization

4-Methoxy benzoic acid (0.76 g) and 2-amino-3-methylpyridine (0.54 g) with 20 ml of acetone was magnetically stirred for 4 h in a round-bottomed flask, and the reaction mixture was kept for slow evaporation. Colourless block-like crystals 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

IUCrData (2016). **1**, x161126 [https://doi.org/10.1107/S2414314616011263]

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Crystal data

$C_6H_9N_2^+·C_8H_7O_3^-$
M_r = 260.29
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 12.2526 (8) Å
b = 6.6872 (3) Å
c = 16.6376 (12) Å
β = 103.836 (4)°
V = 1323.66 (14) Å^3
Z = 4
$F(000)$ = 552
D_x = 1.306 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3853 reflections
θ = 2.0–25.1°
μ = 0.09 mm^{-1}
T = 295 K
Block, colourless
0.26 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.976, T_{max} = 0.982
18167 measured reflections
3737 independent reflections
2223 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 29.7°, θ_{min} = 2.4°
h = −17→17
k = −9→9
l = −20→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.151
S = 1.08
3737 reflections
178 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.4113P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.85075 (14)	0.0076 (3)	0.11668 (11)	0.0415 (4)
C2	0.79234 (15)	−0.1179 (3)	0.15722 (12)	0.0465 (5)
H2	0.7180	−0.0899	0.1573	0.056*
C3	0.84426 (14)	−0.2841 (3)	0.19738 (12)	0.0430 (4)
H3	0.8045	−0.3678	0.2248	0.052*
C4	0.95519 (13)	−0.3300 (2)	0.19798 (10)	0.0340 (4)
C5	1.01214 (14)	−0.2014 (3)	0.15768 (12)	0.0406 (4)
H5	1.0865	−0.2289	0.1575	0.049*
C6	0.96139 (14)	−0.0324 (3)	0.11746 (12)	0.0444 (4)
H6	1.0015	0.0535	0.0912	0.053*
C7	0.8482 (2)	0.3068 (3)	0.03804 (14)	0.0610 (6)
H7A	0.9141	0.3541	0.0769	0.091*
H7B	0.7992	0.4175	0.0183	0.091*
H7C	0.8696	0.2439	−0.0077	0.091*
C8	1.00960 (13)	−0.5140 (3)	0.23994 (11)	0.0377 (4)
C9	0.95005 (15)	−0.0433 (3)	0.38533 (12)	0.0481 (5)
H9	0.8794	0.0128	0.3809	0.058*
C10	0.97554 (17)	−0.2178 (3)	0.42519 (14)	0.0564 (5)
H10	0.9234	−0.2837	0.4482	0.068*
C11	1.08219 (18)	−0.2974 (3)	0.43122 (13)	0.0516 (5)
H11	1.1013	−0.4171	0.4596	0.062*
C12	1.15932 (15)	−0.2059 (3)	0.39696 (11)	0.0403 (4)
C13	1.12801 (13)	−0.0236 (3)	0.35510 (10)	0.0357 (4)
C14	1.27304 (17)	−0.2935 (3)	0.40184 (14)	0.0560 (5)
H14A	1.2828	−0.4106	0.4362	0.084*
H14B	1.3297	−0.1969	0.4252	0.084*
H14C	1.2796	−0.3291	0.3473	0.084*
N1	1.02534 (12)	0.0519 (2)	0.35162 (10)	0.0401 (4)
N2	1.19561 (12)	0.0814 (2)	0.31892 (10)	0.0455 (4)
H2A	1.1728	0.1926	0.2947	0.055*
H2B	1.2620	0.0379	0.3199	0.055*
O1	0.79184 (12)	0.1675 (2)	0.07713 (10)	0.0602 (4)
O2	0.95301 (11)	−0.61756 (19)	0.27896 (10)	0.0536 (4)
O3	1.10690 (10)	−0.55837 (19)	0.23454 (9)	0.0515 (4)
H1	1.0056 (19)	0.169 (2)	0.3269 (14)	0.073 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0378 (9)	0.0431 (10)	0.0424 (10)	0.0075 (8)	0.0071 (8)	0.0015 (8)

C2	0.0307 (8)	0.0560 (11)	0.0548 (12)	0.0073 (8)	0.0142 (8)	0.0037 (9)
C3	0.0325 (8)	0.0477 (10)	0.0517 (11)	−0.0008 (8)	0.0157 (8)	0.0036 (9)
C4	0.0301 (8)	0.0338 (8)	0.0387 (9)	−0.0003 (6)	0.0094 (7)	−0.0040 (7)
C5	0.0286 (8)	0.0437 (10)	0.0514 (11)	0.0021 (7)	0.0134 (7)	0.0013 (8)
C6	0.0365 (9)	0.0461 (10)	0.0528 (12)	−0.0018 (8)	0.0149 (8)	0.0079 (9)
C7	0.0735 (15)	0.0456 (11)	0.0607 (14)	0.0047 (11)	0.0099 (11)	0.0098 (10)
C8	0.0330 (8)	0.0340 (9)	0.0478 (10)	−0.0003 (7)	0.0130 (7)	−0.0042 (8)
C9	0.0357 (9)	0.0589 (12)	0.0514 (12)	−0.0015 (8)	0.0139 (8)	−0.0008 (10)
C10	0.0487 (11)	0.0648 (13)	0.0602 (14)	−0.0108 (10)	0.0219 (10)	0.0088 (11)
C11	0.0584 (12)	0.0463 (11)	0.0507 (12)	−0.0022 (9)	0.0144 (9)	0.0097 (9)
C12	0.0406 (9)	0.0416 (9)	0.0375 (10)	0.0019 (8)	0.0068 (7)	0.0011 (8)
C13	0.0334 (8)	0.0381 (9)	0.0348 (9)	−0.0029 (7)	0.0066 (7)	−0.0037 (7)
C14	0.0520 (11)	0.0566 (12)	0.0598 (13)	0.0170 (10)	0.0138 (10)	0.0111 (10)
N1	0.0356 (7)	0.0402 (8)	0.0450 (9)	0.0013 (6)	0.0106 (6)	0.0010 (7)
N2	0.0344 (7)	0.0430 (8)	0.0615 (11)	0.0054 (6)	0.0166 (7)	0.0108 (7)
O1	0.0490 (8)	0.0609 (9)	0.0712 (10)	0.0175 (7)	0.0152 (7)	0.0210 (8)
O2	0.0435 (7)	0.0443 (7)	0.0809 (11)	0.0060 (6)	0.0302 (7)	0.0153 (7)
O3	0.0378 (7)	0.0470 (7)	0.0757 (10)	0.0092 (6)	0.0255 (7)	0.0111 (7)

Geometric parameters (Å, º)

C1—O1	1.367 (2)	C9—C10	1.341 (3)
C1—C6	1.379 (2)	C9—N1	1.348 (2)
C1—C2	1.379 (3)	C9—H9	0.9300
C2—C3	1.372 (3)	C10—C11	1.392 (3)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.391 (2)	C11—C12	1.360 (3)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.378 (2)	C12—C13	1.411 (2)
C4—C8	1.491 (2)	C12—C14	1.495 (3)
C5—C6	1.383 (2)	C13—N2	1.334 (2)
C5—H5	0.9300	C13—N1	1.344 (2)
C6—H6	0.9300	C14—H14A	0.9600
C7—O1	1.408 (3)	C14—H14B	0.9600
C7—H7A	0.9600	C14—H14C	0.9600
C7—H7B	0.9600	N1—H1	0.888 (9)
C7—H7C	0.9600	N2—H2A	0.8600
C8—O3	1.2525 (19)	N2—H2B	0.8600
C8—O2	1.264 (2)		
O1—C1—C6	124.11 (17)	C10—C9—H9	119.5
O1—C1—C2	115.78 (16)	N1—C9—H9	119.5
C6—C1—C2	120.10 (17)	C9—C10—C11	118.15 (18)
C3—C2—C1	119.77 (16)	C9—C10—H10	120.9
C3—C2—H2	120.1	C11—C10—H10	120.9
C1—C2—H2	120.1	C12—C11—C10	122.14 (19)
C2—C3—C4	121.36 (17)	C12—C11—H11	118.9
C2—C3—H3	119.3	C10—C11—H11	118.9

C4—C3—H3	119.3	C11—C12—C13	117.47 (16)
C5—C4—C3	117.81 (16)	C11—C12—C14	122.21 (18)
C5—C4—C8	121.39 (14)	C13—C12—C14	120.31 (16)
C3—C4—C8	120.79 (15)	N2—C13—N1	117.31 (16)
C4—C5—C6	121.59 (15)	N2—C13—C12	123.54 (15)
C4—C5—H5	119.2	N1—C13—C12	119.14 (15)
C6—C5—H5	119.2	C12—C14—H14A	109.5
C1—C6—C5	119.36 (17)	C12—C14—H14B	109.5
C1—C6—H6	120.3	H14A—C14—H14B	109.5
C5—C6—H6	120.3	C12—C14—H14C	109.5
O1—C7—H7A	109.5	H14A—C14—H14C	109.5
O1—C7—H7B	109.5	H14B—C14—H14C	109.5
H7A—C7—H7B	109.5	C13—N1—C9	122.09 (16)
O1—C7—H7C	109.5	C13—N1—H1	119.9 (16)
H7A—C7—H7C	109.5	C9—N1—H1	118.0 (16)
H7B—C7—H7C	109.5	C13—N2—H2A	120.0
O3—C8—O2	123.74 (16)	C13—N2—H2B	120.0
O3—C8—C4	119.25 (15)	H2A—N2—H2B	120.0
O2—C8—C4	117.00 (14)	C1—O1—C7	118.63 (15)
C10—C9—N1	120.98 (18)		

O1—C1—C2—C3	178.87 (17)	N1—C9—C10—C11	0.4 (3)
C6—C1—C2—C3	−0.9 (3)	C9—C10—C11—C12	−1.2 (3)
C1—C2—C3—C4	−0.2 (3)	C10—C11—C12—C13	0.7 (3)
C2—C3—C4—C5	0.8 (3)	C10—C11—C12—C14	−178.7 (2)
C2—C3—C4—C8	−178.34 (17)	C11—C12—C13—N2	179.89 (17)
C3—C4—C5—C6	−0.3 (3)	C14—C12—C13—N2	−0.8 (3)
C8—C4—C5—C6	178.86 (17)	C11—C12—C13—N1	0.7 (3)
O1—C1—C6—C5	−178.34 (18)	C14—C12—C13—N1	−179.99 (17)
C2—C1—C6—C5	1.4 (3)	N2—C13—N1—C9	179.22 (16)
C4—C5—C6—C1	−0.8 (3)	C12—C13—N1—C9	−1.5 (3)
C5—C4—C8—O3	−4.0 (3)	C10—C9—N1—C13	1.0 (3)
C3—C4—C8—O3	175.11 (17)	C6—C1—O1—C7	−3.4 (3)
C5—C4—C8—O2	176.43 (17)	C2—C1—O1—C7	176.88 (18)
C3—C4—C8—O2	−4.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.89 (1)	1.69 (1)	2.573 (2)	174 (2)
N2—H2*A*···O3^{i}	0.86	2.01	2.8680 (19)	175
N2—H2*B*···O3^{ii}	0.86	2.12	2.924 (2)	155
C2—H2···O2^{iii}	0.93	2.57	3.419 (2)	152
C10—H10···O1^{iv}	0.93	2.59	3.356 (2)	140

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+5/2, *y*+1/2, −*z*+1/2; (iii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iv) −*x*+3/2, *y*−1/2, −*z*+1/2.