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ISSN 2414-3146

Dimethyl 2,7-di-*tert*-butylpyrene-4,9-dicarboxylate

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Received 16 February 2026
Accepted 9 March 2026

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

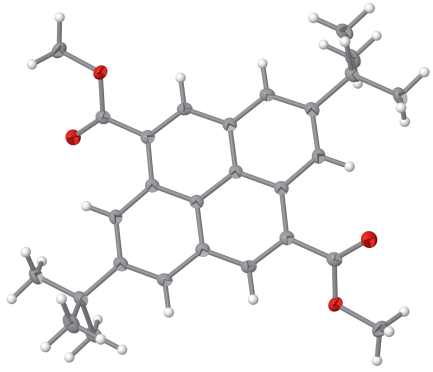
Keywords: crystal structure; polyaromatic hydrocarbon; pyrene dicarboxylic acid; dimethylester.

CCDC reference: 2535992

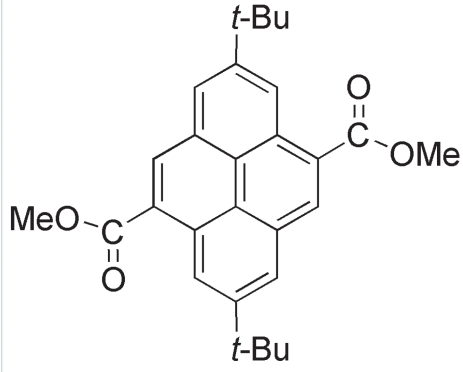
Structural data: full structural data are available from iucrdata.iucr.org

The complete molecule of the title compound, $C_{28}H_{30}O_4$, is generated by a crystallographic centre of symmetry and the ester moiety is twisted away from the fused-ring plane by 28.03 (8)° due to steric repulsion. In the crystal, a weak C—H···O hydrogen bond links the molecules into (001) sheets.

3D view



Chemical scheme



Structure description

In recent years, polycyclic aromatic hydrocarbons (PAHs) have attracted great interest owing to their significant photochemical and electrical properties (Dötz *et al.*, 2000). In PAHs, pyrene is the most studied and an important class of polyaromatic hydrocarbon found in charcoal. Pyrene and its substituted derivatives have *p*-type semiconductor properties (Moriguchi *et al.*, 2017). We reported substituted pyrene derivatives (Moriguchi *et al.*, 2018) and we have also studied a lanthanide complex having four pyrene moieties (Moriguchi *et al.*, 2014) in order to evaluate its fluorescence property.

As part of our ongoing studies of these systems, we now report the synthesis and crystal structure of the title compound, $C_{28}H_{30}O_4$ (**I**). The complete molecule (Fig. 1) is generated by a crystallographic centre of symmetry in the orthorhombic space group *Pbca* at the mid-point of the C6—C6^{i} [symmetry code: (i) $-x, 1-y, 2-z$] bond. The C12 methyl group lies almost in the plane of the fused ring system, whereas C10 and C11 are equally displaced either side [deviations = 0.001 (2), −1.290 (2) and 1.210 (2) Å, respectively]. The twist angle between the fused ring system and the C13/O1/O2/C14 ester moiety is 28.03 (8)°. This twist appears to arise due to steric repulsion between the O atoms of the ester group and hydrogen atoms of the pyrene ring system (H7···O1 = 2.27 Å; H3···O2 = 2.36 Å).

The packing of (**I**) is shown in Fig. 2. No intermolecular π–π stacking interactions between the pyrene rings are observed, but some short intermolecular contacts can be detected (Fig. 3), including a weak C1—H1···O1^{ii} [symmetry code: (ii) $= -\frac{1}{2}+x, \frac{3}{2}-y,$

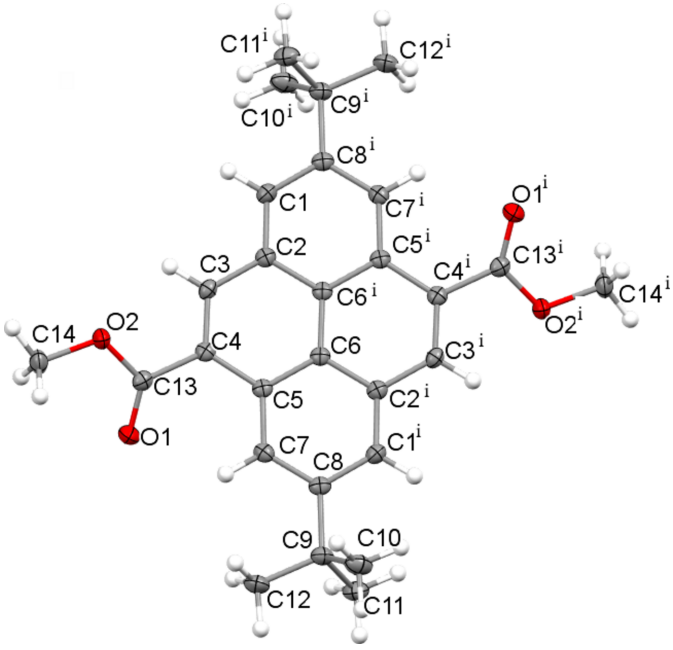


Figure 1
The molecular structure of (**I**) with displacement ellipsoids shown at the 50% probability level. Symmetry code: (i) $-x, 1-y, 2-z$.

$2-z$] hydrogen bond with H···O = 2.32 Å and C—H···O = 164°, which links the molecules into (001) sheets.

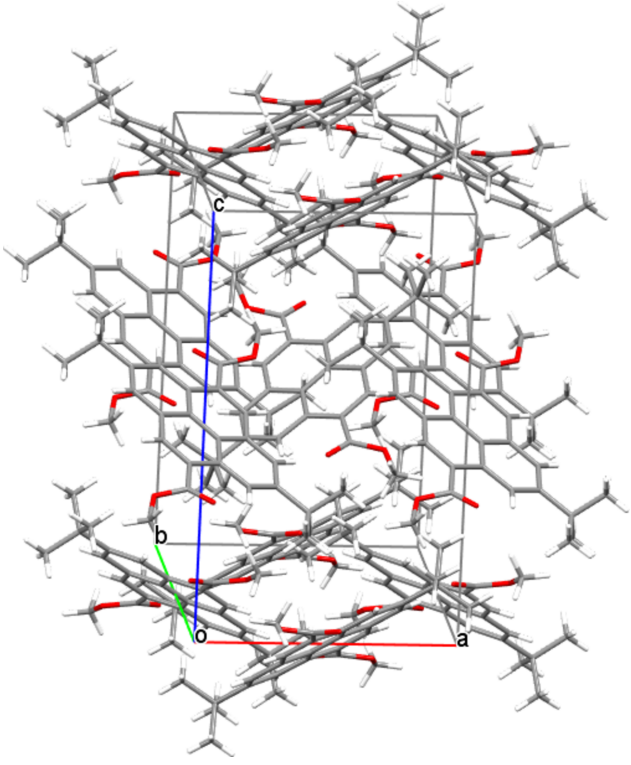


Figure 2
Crystal packing of (**I**).

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{28}H_{30}O_4$
M_r	430.52
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	90
a, *b*, *c* (Å)	9.9087 (10), 13.7094 (14), 16.7900 (17)
V (Å^3)	2280.8 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.40 × 0.35 × 0.30
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.663, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20373, 2009, 1686
R_{int}	0.047
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.092, 1.06
No. of reflections	2009
No. of parameters	149
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.20

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS* (Sheldrick, 2008), *SHELXL2019/3* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

NaOH (5.00 mmol) was added to an absolute methanol solution (50 ml) of 2,7-di-*t*-butylpyrene-4,9-dicarboxylic acid (1.00 mmol) at room temperature. The reaction mixture was stirred for 10 h at 318 K. After completion of reaction, the resultant mixture was cooled to room temperature, then poured into ice-cold water. The precipitate was separated by

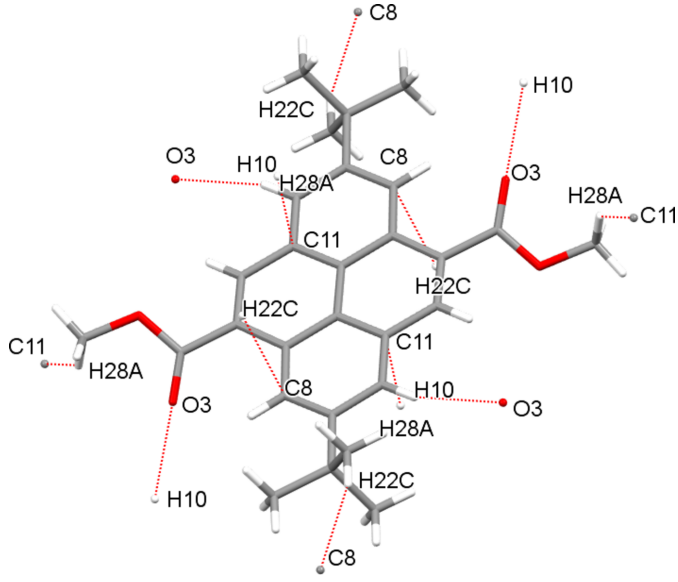


Figure 3
Intermolecular short contacts in the crystal of (**I**).

filtration and then washed with cold water. The resulting precipitate was filtered and recrystallized from methanol solution. Single crystals of (**I**) suitable for X-ray analysis were obtained by slow evaporation of dichloromethane solution at room temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

We are grateful to the Center for Instrumental Analysis, Kyushu Institute of Technology (KITCIA) for the X-ray analysis.

References

Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Dötz, F., Brand, D. J., Ito, S., Gherghel, L. & Müllen, K. (2000). *J. Am. Chem. Soc.* **122**, 7707–7717.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Moriguchi, T., Higashi, M., Yakeya, D., Jalli, V., Tsuge, A., Okauchi, T., Nagamatsu, S. & Takashima, W. (2017). *J. Mol. Struct.* **1127**, 413–418.
Moriguchi, T., Yakeya, D., Tsuge, A. & Jalli, V. (2018). *J. Mol. Struct.* **1157**, 348–354.
Moriguchi, T., Yoza, K. & Tsuge, A. (2014). *J. Crystallogr.* Article ID 271238.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2026). **11**, x260248 [https://doi.org/10.1107/S2414314626002488]

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Crystal data

$C_{28}H_{30}O_4$
M_r = 430.52
Orthorhombic, *Pbca*
a = 9.9087 (10) Å
b = 13.7094 (14) Å
c = 16.7900 (17) Å
V = 2280.8 (4) Å^3
Z = 4
F(000) = 920
D_x = 1.254 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4114 reflections
θ = 2.8–26.5°
μ = 0.08 mm^{-1}
T = 90 K
Prism, clear light yellow
0.40 × 0.35 × 0.30 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.663, T_{max} = 0.746
20373 measured reflections
2009 independent reflections
1686 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 25.0°, θ_{min} = 2.8°
h = −11→11
k = −16→16
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 1.06
2009 reflections
149 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.9455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.00597 (11)	0.82315 (7)	0.89804 (6)	0.0251 (3)
O2	−0.22549 (10)	0.78601 (7)	0.90258 (6)	0.0213 (3)
C1	−0.27651 (14)	0.50355 (11)	1.08192 (8)	0.0182 (3)
H1	−0.354287	0.542997	1.089500	0.022*
C2	−0.17052 (14)	0.53904 (10)	1.03565 (8)	0.0166 (3)
C3	−0.17815 (15)	0.63220 (10)	0.99780 (8)	0.0173 (3)
H3	−0.257346	0.670314	1.004777	0.021*
C4	−0.07638 (14)	0.66847 (10)	0.95215 (8)	0.0165 (3)
C5	0.04671 (14)	0.61282 (10)	0.94065 (8)	0.0155 (3)
C6	0.05351 (14)	0.51869 (10)	0.97619 (8)	0.0149 (3)
C7	0.15649 (14)	0.64500 (10)	0.89476 (8)	0.0171 (3)
H7	0.152365	0.707844	0.871049	0.021*
C8	0.27134 (14)	0.58810 (10)	0.88272 (8)	0.0173 (3)
C9	0.39102 (15)	0.62209 (11)	0.83199 (9)	0.0200 (3)
C10	0.41008 (17)	0.55038 (12)	0.76256 (9)	0.0278 (4)
H10A	0.329155	0.550616	0.729009	0.042*
H10B	0.424908	0.484584	0.783640	0.042*
H10C	0.488348	0.570193	0.730754	0.042*
C11	0.51910 (15)	0.62302 (12)	0.88319 (9)	0.0262 (4)
H11A	0.596640	0.641106	0.850099	0.039*
H11B	0.533827	0.558011	0.905842	0.039*
H11C	0.508712	0.670556	0.926348	0.039*
C12	0.36998 (16)	0.72414 (11)	0.79755 (10)	0.0262 (4)
H12A	0.289826	0.724224	0.763359	0.039*
H12B	0.449211	0.742784	0.766115	0.039*
H12C	0.357403	0.770847	0.841110	0.039*
C13	−0.09487 (14)	0.76657 (10)	0.91529 (8)	0.0178 (3)
C14	−0.25447 (16)	0.88024 (11)	0.86837 (9)	0.0252 (4)
H14A	−0.223178	0.931577	0.904554	0.038*
H14B	−0.351987	0.886744	0.860213	0.038*
H14C	−0.207928	0.886423	0.817121	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0216 (6)	0.0183 (6)	0.0356 (6)	−0.0033 (5)	0.0012 (5)	0.0032 (5)
O2	0.0196 (6)	0.0175 (5)	0.0268 (6)	0.0018 (4)	−0.0005 (4)	0.0051 (4)
C1	0.0155 (8)	0.0204 (8)	0.0189 (7)	0.0011 (6)	0.0002 (6)	−0.0021 (6)
C2	0.0165 (7)	0.0187 (8)	0.0145 (7)	−0.0011 (6)	−0.0019 (6)	−0.0022 (6)
C3	0.0157 (7)	0.0192 (8)	0.0169 (7)	0.0020 (6)	−0.0014 (6)	−0.0029 (6)
C4	0.0168 (7)	0.0174 (8)	0.0152 (7)	−0.0016 (6)	−0.0027 (6)	−0.0024 (6)
C5	0.0153 (7)	0.0178 (7)	0.0133 (7)	−0.0022 (6)	−0.0027 (6)	−0.0027 (6)
C6	0.0152 (7)	0.0170 (7)	0.0126 (7)	−0.0022 (6)	−0.0028 (5)	−0.0023 (5)
C7	0.0185 (8)	0.0177 (7)	0.0152 (7)	−0.0028 (6)	−0.0029 (6)	0.0006 (6)
C8	0.0164 (7)	0.0212 (8)	0.0143 (7)	−0.0032 (6)	−0.0012 (6)	−0.0025 (6)

C9	0.0185 (8)	0.0222 (8)	0.0194 (7)	−0.0033 (6)	0.0030 (6)	−0.0007 (6)
C10	0.0302 (9)	0.0299 (9)	0.0233 (8)	−0.0065 (7)	0.0085 (7)	−0.0022 (7)
C11	0.0185 (8)	0.0330 (9)	0.0270 (8)	−0.0046 (7)	0.0017 (6)	0.0014 (7)
C12	0.0246 (9)	0.0268 (9)	0.0273 (9)	−0.0044 (7)	0.0068 (7)	0.0053 (7)
C13	0.0176 (8)	0.0195 (8)	0.0164 (7)	−0.0003 (6)	0.0002 (6)	−0.0039 (6)
C14	0.0291 (9)	0.0189 (8)	0.0277 (8)	0.0067 (7)	0.0018 (7)	0.0040 (6)

Geometric parameters (Å, º)

O1—C13	1.2088 (17)	C8—C9	1.533 (2)
O2—C13	1.3386 (17)	C9—C10	1.537 (2)
O2—C14	1.4426 (17)	C9—C11	1.533 (2)
C1—H1	0.9500	C9—C12	1.528 (2)
C1—C2	1.394 (2)	C10—H10A	0.9800
C1—C8^{i}	1.391 (2)	C10—H10B	0.9800
C2—C3	1.428 (2)	C10—H10C	0.9800
C2—C6^{i}	1.418 (2)	C11—H11A	0.9800
C3—H3	0.9500	C11—H11B	0.9800
C3—C4	1.361 (2)	C11—H11C	0.9800
C4—C5	1.452 (2)	C12—H12A	0.9800
C4—C13	1.492 (2)	C12—H12B	0.9800
C5—C6	1.423 (2)	C12—H12C	0.9800
C5—C7	1.404 (2)	C14—H14A	0.9800
C6—C6^{i}	1.424 (3)	C14—H14B	0.9800
C7—H7	0.9500	C14—H14C	0.9800
C7—C8	1.394 (2)		
C13—O2—C14	115.73 (11)	C12—C9—C10	108.40 (12)
C2—C1—H1	119.1	C12—C9—C11	108.51 (12)
C8^{i}—C1—H1	119.1	C9—C10—H10A	109.5
C8^{i}—C1—C2	121.70 (13)	C9—C10—H10B	109.5
C1—C2—C3	121.34 (13)	C9—C10—H10C	109.5
C1—C2—C6^{i}	119.96 (13)	H10A—C10—H10B	109.5
C6^{i}—C2—C3	118.69 (13)	H10A—C10—H10C	109.5
C2—C3—H3	118.7	H10B—C10—H10C	109.5
C4—C3—C2	122.55 (13)	C9—C11—H11A	109.5
C4—C3—H3	118.7	C9—C11—H11B	109.5
C3—C4—C5	120.37 (13)	C9—C11—H11C	109.5
C3—C4—C13	118.17 (13)	H11A—C11—H11B	109.5
C5—C4—C13	121.46 (12)	H11A—C11—H11C	109.5
C6—C5—C4	117.42 (12)	H11B—C11—H11C	109.5
C7—C5—C4	123.98 (13)	C9—C12—H12A	109.5
C7—C5—C6	118.57 (13)	C9—C12—H12B	109.5
C2^{i}—C6—C5	119.08 (13)	C9—C12—H12C	109.5
C2^{i}—C6—C6^{i}	119.14 (16)	H12A—C12—H12B	109.5
C5—C6—C6^{i}	121.78 (16)	H12A—C12—H12C	109.5
C5—C7—H7	118.8	H12B—C12—H12C	109.5
C8—C7—C5	122.42 (13)	O1—C13—O2	122.59 (13)

C8—C7—H7	118.8	O1—C13—C4	126.04 (13)
C1^{i}—C8—C7	118.27 (13)	O2—C13—C4	111.37 (12)
C1^{i}—C8—C9	118.91 (13)	O2—C14—H14A	109.5
C7—C8—C9	122.82 (13)	O2—C14—H14B	109.5
C8—C9—C10	108.80 (12)	O2—C14—H14C	109.5
C8—C9—C11	109.36 (12)	H14A—C14—H14B	109.5
C11—C9—C10	109.21 (13)	H14A—C14—H14C	109.5
C12—C9—C8	112.52 (12)	H14B—C14—H14C	109.5
C1—C2—C3—C4	−179.81 (13)	C5—C7—C8—C1^{i}	−0.3 (2)
C1^{i}—C8—C9—C10	59.99 (17)	C5—C7—C8—C9	179.30 (12)
C1^{i}—C8—C9—C11	−59.22 (17)	C6^{i}—C2—C3—C4	−1.3 (2)
C1^{i}—C8—C9—C12	−179.88 (13)	C6—C5—C7—C8	0.1 (2)
C2—C3—C4—C5	−0.6 (2)	C7—C5—C6—C2^{i}	0.20 (19)
C2—C3—C4—C13	179.95 (12)	C7—C5—C6—C6^{i}	179.69 (15)
C3—C4—C5—C6	2.36 (19)	C7—C8—C9—C10	−119.65 (15)
C3—C4—C5—C7	−179.79 (13)	C7—C8—C9—C11	121.14 (15)
C3—C4—C13—O1	152.38 (14)	C7—C8—C9—C12	0.48 (19)
C3—C4—C13—O2	−27.83 (18)	C8^{i}—C1—C2—C3	178.31 (13)
C4—C5—C6—C2^{i}	178.17 (12)	C8^{i}—C1—C2—C6^{i}	−0.1 (2)
C4—C5—C6—C6^{i}	−2.3 (2)	C13—C4—C5—C6	−178.16 (12)
C4—C5—C7—C8	−177.69 (13)	C13—C4—C5—C7	−0.3 (2)
C5—C4—C13—O1	−27.1 (2)	C14—O2—C13—O1	−1.3 (2)
C5—C4—C13—O2	152.68 (12)	C14—O2—C13—C4	178.87 (11)

Symmetry code: (i) −*x*, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O1^{ii}	0.95	2.38	3.3057 (18)	164

Symmetry code: (ii) *x*−1/2, −*y*+3/2, −*z*+2.