

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(Z)-Methyl 2-bromomethyl-3-(2-chlorophenyl)acrylateR. Madhanraj,^a S. Vijayakumar,^b R. Selvakumar,^c
M. Bakthadoss^c and S. Murugavel^{d*}^aDepartment of Physics, Ranipettai Engineering College, Thenkadathangal, Walaja 632 513, India, ^bDepartment of Physics, Sri Balaji Chokkalingam Engineering College, Arni, Thiruvannamalai 632 317, India, ^cDepartment of Organic Chemistry, University of Madras, Maraimalai Campus, Chennai 600 025, India, and ^dDepartment of Physics, Thanthai Periyar Government Institute of Technology, Vellore 632 002, India

Correspondence e-mail: smurugavel27@gmail.com

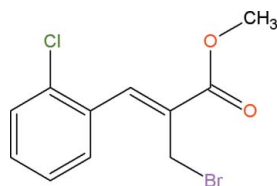
Received 10 September 2011; accepted 27 September 2011

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.034; wR factor = 0.089; data-to-parameter ratio = 24.4.

In the title compound, $\text{C}_{11}\text{H}_{10}\text{BrClO}_2$, the dihedral angle between the benzene ring and the plane of the acrylate unit is $62.1(1)^\circ$. The crystal packing is stabilized by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and $\text{C}-\text{Cl}\cdots\pi$ interactions [$\text{Cl}\cdots\text{centroid} = 3.829(1)$ Å and $\text{C}-\text{Cl}\cdots\text{centroid} = 165.3(1)^\circ$].

Related literature

For background to the applications of acrylates, see: de Fraine & Martin (1991); Zhang & Ji (1992). For related structures, see: Wang *et al.* (2011); Ren *et al.* (2008). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_{10}\text{BrClO}_2$
 $M_r = 289.55$ Monoclinic, $P2_1/c$
 $a = 10.0657(7)$ Å $b = 10.2174(7)$ Å
 $c = 11.3598(7)$ Å
 $\beta = 97.649(2)^\circ$
 $V = 1157.91(13)$ Å³
 $Z = 4$ Mo $K\alpha$ radiation
 $\mu = 3.76$ mm⁻¹
 $T = 293$ K
 $0.24 \times 0.22 \times 0.16$ mm

Data collection

Bruker APEXII CCD
diffractometer
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)
 $T_{\min} = 0.390$, $T_{\max} = 0.548$ 14580 measured reflections
3336 independent reflections
2139 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.089$
 $S = 0.99$
3336 reflections137 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.57$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.54$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2}\cdots\text{O1}^i$	0.93	2.48	3.373 (3)	162

Symmetry code: (i) $x - 1, y, z$.

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

SM thank Dr Babu Vargheese, SAIF, IIT, Madras, India, for his help with the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2189).

References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555-1573.
- Bruker (2004). APEX2, SAINT and XPREP. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fraine, P. J. de & Martin, A. (1991). US Patent No. 5 055 471.
- Ren, X.-L., Zhang, H.-R., Wang, W.-D., Tao, R.-J. & He, H.-W. (2008). *Acta Cryst.* **E64**, o6.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112-122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148-155.
- Wang, L., Meng, F.-Y., Lin, C.-W., Chen, H.-Y. & Luo, X. (2011). *Acta Cryst.* **E67**, o354.
- Zhang, L. P. & Ji, Z. Z. (1992). *Acta Pharm. Sin.* **27**, 817-823.

supporting information

Acta Cryst. (2011). E67, o2812 [https://doi.org/10.1107/S1600536811039663]

(Z)-Methyl 2-bromomethyl-3-(2-chlorophenyl)acrylate

R. Madhanraj, S. Vijayakumar, R. Selvakumar, M. Bakthadoss and S. Murugavel

S1. Comment

Acrylate and its derivatives are important compounds because of their agrochemical and medical applications (de Fraine *et al.*, 1991; Zhang & Ji, 1992). We report herein the crystal structure of the title compound (Fig. 1). The acrylate plane (C7/C8/C10/C11/O1/O2) forms a dihedral angle of 62.1 (1)° with the benzene ring (C1—C6). The geometric parameters of the title molecule agree well with those reported for similar structures (Wang *et al.*, 2011, Ren *et al.*, 2008).

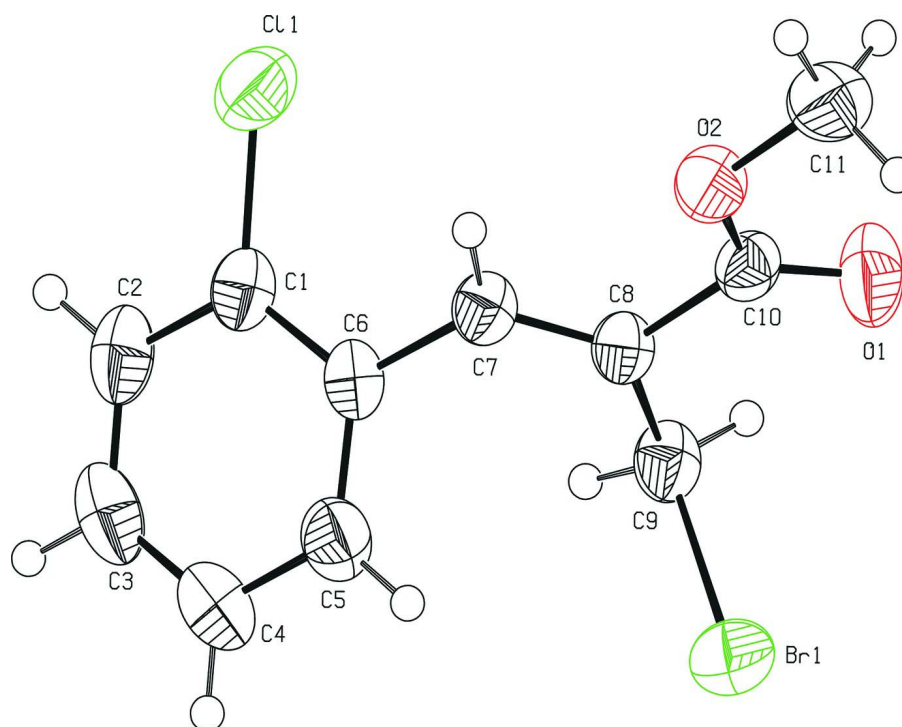
The molecule is stabilized by weak intramolecular C7—H7···O2 hydrogen bond which generates an S(5) ring motif (Bernstein *et al.*, 1995). The crystal packing is stabilized by intermolecular C—H···O hydrogen bonds. Atom C2 in the molecule at (x, y, z) donates one proton to atom O1 at (-I+x, y, z), forming a C(8) chain along the a axis (Fig. 2). The crystal packing is further stabilized by C—Cl··· π interactions involving chlorine Cl1 and benzene ring (C1—C6), with a Cl···centroid(Cgⁱⁱ) distance of 3.829 (1) Å and a C1—Cl1···Cgⁱⁱ angle of 165.3 (1)° (symmetry code as in Fig. 2).

S2. Experimental

To a stirred solution of methyl 2-((2-chlorophenyl)(hydroxy)methyl)acrylate (4.42 mmol, 1 g) in dichloro methane (DCM) was added a 48% hydrobromic acid (8.84 mmol, 0.71 g) solution and then a concentrated sulphuric acid solution (catalytic amount) at 273 K. After stirring overnight at room temperature, the mixture was diluted with DCM and water. The aqueous phase was extracted twice with DCM. The combined organic phase was washed twice with water and then dried with sodium sulphate. Removal of the solvent led to the crude product which was purified through a pad of silica gel (100—200 mesh) using ethylacetate and hexanes (1:9) as solvents. The pure title compound was obtained as a colorless solid (1.14 g, 90%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an ethylacetate solution at room temperature.

S3. Refinement

All the H atoms were positioned geometrically, with C—H = 0.93 - 0.98 Å and constrained to ride on their parent atom, with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

**Figure 1**

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

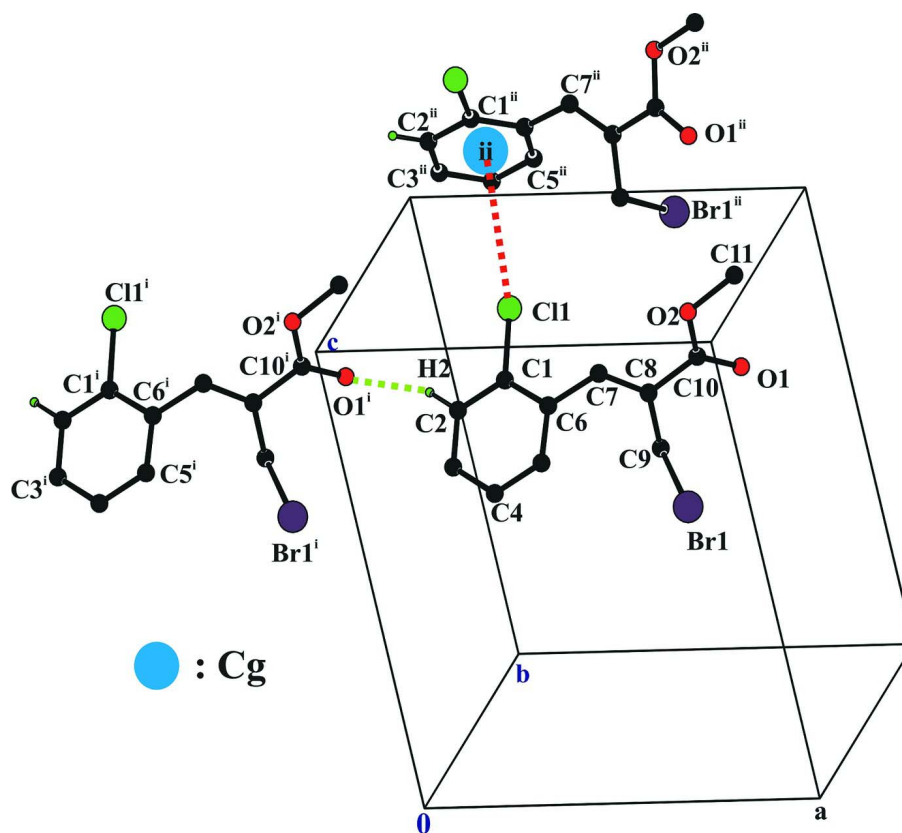


Figure 2

A view of the intermolecular C—H...O and C—Cl... π interactions (dotted lines) in the crystal structure of the title compound. H atoms not involved in intermolecular interactions were omitted. Cg denotes centroid of the C1—C6 benzene ring [Symmetry code: (i) $-I+x, y, z$; (ii) $x, 1/2-y, 1/2+z$.]

(Z)-Methyl 2-bromomethyl-3-(2-chlorophenyl)acrylate

Crystal data

$C_{11}H_{10}BrClO_2$
 $M_r = 289.55$
 Monoclinic, $P2_1/c$
 Hall symbol: $-P 2ybc$
 $a = 10.0657 (7) \text{ \AA}$
 $b = 10.2174 (7) \text{ \AA}$
 $c = 11.3598 (7) \text{ \AA}$
 $\beta = 97.649 (2)^\circ$
 $V = 1157.91 (13) \text{ \AA}^3$
 $Z = 4$

$F(000) = 576$
 $D_x = 1.661 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 3345 reflections
 $\theta = 2.0\text{--}29.9^\circ$
 $\mu = 3.76 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Block, yellow
 $0.24 \times 0.22 \times 0.16 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: $10.0 \text{ pixels mm}^{-1}$
 ω scans

Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.390, T_{\max} = 0.548$
 14580 measured reflections
 3336 independent reflections
 2139 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

$\theta_{\max} = 29.9^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -14 \rightarrow 14$

$k = -14 \rightarrow 14$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.089$
 $S = 0.99$
 3336 reflections
 137 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.4461P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.57 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{Å}^{-3}$

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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.83211 (3)	0.03430 (3)	0.63091 (2)	0.06228 (12)
Cl1	0.43126 (7)	0.24881 (8)	1.00168 (6)	0.06382 (19)
O2	0.91325 (15)	0.14097 (17)	1.01998 (13)	0.0471 (4)
C1	0.4117 (2)	0.1427 (2)	0.8812 (2)	0.0437 (5)
C6	0.5234 (2)	0.0869 (2)	0.84130 (19)	0.0391 (5)
C7	0.6602 (2)	0.1162 (2)	0.89910 (19)	0.0381 (5)
H7	0.6767	0.1091	0.9814	0.046*
C8	0.7621 (2)	0.1522 (2)	0.84211 (18)	0.0358 (4)
C10	0.8961 (2)	0.1833 (2)	0.90868 (18)	0.0387 (5)
O1	0.98111 (17)	0.2408 (2)	0.86463 (16)	0.0634 (5)
C9	0.7514 (2)	0.1773 (2)	0.71290 (19)	0.0439 (5)
H9A	0.7964	0.2589	0.6994	0.053*
H9B	0.6578	0.1863	0.6804	0.053*
C5	0.4999 (3)	0.0026 (2)	0.7449 (2)	0.0504 (6)
H5	0.5724	-0.0379	0.7171	0.061*
C2	0.2834 (2)	0.1184 (3)	0.8258 (2)	0.0552 (6)
H2	0.2102	0.1580	0.8533	0.066*
C3	0.2648 (3)	0.0354 (3)	0.7298 (3)	0.0602 (7)
H3	0.1786	0.0187	0.6922	0.072*
C11	1.0420 (2)	0.1709 (3)	1.0877 (2)	0.0585 (7)
H11A	1.1113	0.1245	1.0547	0.088*
H11B	1.0416	0.1447	1.1688	0.088*
H11C	1.0583	0.2633	1.0845	0.088*

C4	0.3727 (3)	-0.0228 (3)	0.6893 (3)	0.0576 (7)
H4	0.3599	-0.0792	0.6246	0.069*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.06623 (19)	0.0758 (2)	0.04610 (15)	-0.00412 (14)	0.01240 (12)	-0.01212 (13)
Cl1	0.0517 (4)	0.0854 (5)	0.0558 (4)	0.0079 (3)	0.0125 (3)	-0.0115 (3)
O2	0.0394 (8)	0.0644 (11)	0.0359 (8)	0.0020 (8)	-0.0008 (6)	-0.0001 (7)
C1	0.0385 (11)	0.0485 (14)	0.0449 (12)	0.0006 (10)	0.0091 (9)	0.0080 (10)
C6	0.0320 (10)	0.0409 (12)	0.0442 (11)	-0.0023 (9)	0.0042 (8)	0.0075 (10)
C7	0.0343 (10)	0.0416 (13)	0.0381 (10)	0.0038 (9)	0.0032 (8)	0.0036 (9)
C8	0.0309 (10)	0.0375 (12)	0.0383 (10)	0.0040 (9)	0.0023 (8)	0.0034 (9)
C10	0.0333 (10)	0.0448 (13)	0.0380 (10)	0.0053 (9)	0.0053 (8)	-0.0013 (9)
O1	0.0381 (9)	0.0980 (15)	0.0530 (10)	-0.0153 (9)	0.0023 (7)	0.0131 (10)
C9	0.0365 (11)	0.0537 (14)	0.0406 (11)	0.0007 (10)	0.0015 (9)	0.0071 (10)
C5	0.0447 (13)	0.0450 (14)	0.0617 (15)	-0.0032 (11)	0.0073 (11)	-0.0004 (11)
C2	0.0329 (11)	0.0706 (18)	0.0627 (15)	0.0017 (12)	0.0087 (10)	0.0129 (14)
C3	0.0400 (13)	0.0667 (18)	0.0700 (17)	-0.0132 (13)	-0.0064 (12)	0.0111 (14)
C11	0.0447 (13)	0.082 (2)	0.0447 (13)	0.0099 (13)	-0.0091 (10)	-0.0104 (13)
C4	0.0533 (15)	0.0524 (16)	0.0642 (16)	-0.0124 (13)	-0.0026 (12)	-0.0010 (13)

Geometric parameters (Å, °)

Br1—C9	1.966 (2)	C9—H9A	0.9700
Cl1—C1	1.737 (3)	C9—H9B	0.9700
O2—C10	1.326 (3)	C5—C4	1.375 (4)
O2—C11	1.449 (3)	C5—H5	0.9300
C1—C2	1.381 (3)	C2—C3	1.375 (4)
C1—C6	1.389 (3)	C2—H2	0.9300
C6—C5	1.389 (4)	C3—C4	1.371 (4)
C6—C7	1.475 (3)	C3—H3	0.9300
C7—C8	1.336 (3)	C11—H11A	0.9600
C7—H7	0.9300	C11—H11B	0.9600
C8—C9	1.480 (3)	C11—H11C	0.9600
C8—C10	1.490 (3)	C4—H4	0.9300
C10—O1	1.201 (3)		
C10—O2—C11	115.55 (19)	Br1—C9—H9B	109.4
C2—C1—C6	121.7 (2)	H9A—C9—H9B	108.0
C2—C1—Cl1	118.14 (19)	C4—C5—C6	121.9 (3)
C6—C1—Cl1	120.10 (18)	C4—C5—H5	119.0
C1—C6—C5	116.9 (2)	C6—C5—H5	119.0
C1—C6—C7	121.3 (2)	C3—C2—C1	119.5 (2)
C5—C6—C7	121.8 (2)	C3—C2—H2	120.3
C8—C7—C6	124.9 (2)	C1—C2—H2	120.3
C8—C7—H7	117.6	C4—C3—C2	120.2 (2)
C6—C7—H7	117.6	C4—C3—H3	119.9

C7—C8—C9	124.71 (19)	C2—C3—H3	119.9
C7—C8—C10	120.97 (19)	O2—C11—H11A	109.5
C9—C8—C10	114.06 (18)	O2—C11—H11B	109.5
O1—C10—O2	123.2 (2)	H11A—C11—H11B	109.5
O1—C10—C8	122.7 (2)	O2—C11—H11C	109.5
O2—C10—C8	114.11 (18)	H11A—C11—H11C	109.5
C8—C9—Br1	111.16 (15)	H11B—C11—H11C	109.5
C8—C9—H9A	109.4	C3—C4—C5	119.7 (3)
Br1—C9—H9A	109.4	C3—C4—H4	120.2
C8—C9—H9B	109.4	C5—C4—H4	120.2
C2—C1—C6—C5	-1.7 (3)	C7—C8—C10—O2	16.2 (3)
C11—C1—C6—C5	179.72 (18)	C9—C8—C10—O2	-169.36 (19)
C2—C1—C6—C7	178.3 (2)	C7—C8—C9—Br1	-106.0 (2)
C11—C1—C6—C7	-0.2 (3)	C10—C8—C9—Br1	79.8 (2)
C1—C6—C7—C8	-130.5 (2)	C1—C6—C5—C4	1.4 (4)
C5—C6—C7—C8	49.6 (3)	C7—C6—C5—C4	-178.6 (2)
C6—C7—C8—C9	4.5 (4)	C6—C1—C2—C3	1.1 (4)
C6—C7—C8—C10	178.3 (2)	C11—C1—C2—C3	179.6 (2)
C11—O2—C10—O1	1.2 (3)	C1—C2—C3—C4	0.0 (4)
C11—O2—C10—C8	-179.3 (2)	C2—C3—C4—C5	-0.3 (4)
C7—C8—C10—O1	-164.3 (2)	C6—C5—C4—C3	-0.5 (4)
C9—C8—C10—O1	10.1 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C7—H7 \cdots O2	0.93	2.39	2.740 (3)	102
C2—H2 \cdots O1 ⁱ	0.93	2.48	3.373 (3)	162

Symmetry code: (i) $x-1, y, z$.