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Benzyl 3-(10-oxo-9,10-dihydrophenanthren-9-ylidene)dithiocarbazate

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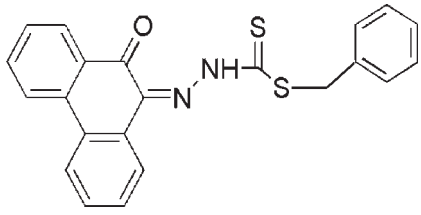
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.098; data-to-parameter ratio = 13.6.

In the title compound, $C_{22}H_{16}N_2OS_2$, the phenanthrene ring is nearly perpendicular to the phenyl ring, making a dihedral angle of 87.2 (2)°. Intramolecular N—H···O interactions are present. In the crystal structure, the molecules are linked through intermolecular C—H···O interactions. The crystal structure is also stabilized by C—H···π interactions and weak π–π contacts [centroid-centroid distance = 3.36 (6) Å].

Related literature

For the biological properties of Schiff bases, see: Bhandari *et al.* (2008). Recently, some Schiff bases derived from the reaction of *S*-benzyldithiocarbazate with aldehydes or ketones have been reported, see: Ali *et al.* (2003*a*,*b*); How *et al.* (2007); Tarafder *et al.* (2008); Zhou *et al.* (2002). For the synthesis of *S*-benzyldithiocarbazate, see: Chew *et al.* (2004). For the synthesis of the title compound, see: Ali *et al.* (2004).



Experimental

Crystal data

$C_{22}H_{16}N_2OS_2$
M_r = 388.49
Monoclinic, $P2_1/c$
a = 14.4945 (19) Å
b = 5.6978 (7) Å
c = 22.816 (3) Å
β = 93.610 (2)°
V = 1880.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 296 K
0.30 × 0.30 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.916, T_{max} = 0.943
9220 measured reflections
3316 independent reflections
2638 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.098
S = 1.06
3316 reflections
244 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1	0.86	1.89	2.560 (2)	134
C12—H12···O1^{i}	0.93	2.42	3.239 (2)	147
C5—H5···$Cg1^{ii}$	0.93	2.76	3.559 (2)	144

Symmetry codes: (i) $-x, -y+3, -z$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$. $Cg1$ is the centroid of the C2–C7 ring.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: HG2573).

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S1. Comment

Schiff bases are versatile compounds which possess excellent biologically properties (Bhandari *et al.*,2008). Recently, some Schiff bases derived from the reaction of *S*-benzyldithiocarbazate with aldehydes or ketones have been reported (Zhou *et al.*, 2002; Ali *et al.*, 2003*a*,b; How *et al.*, 2007; Tarafder *et al.*, 2008). We synthesized the title compound ((Fig. 1)) and report herein its crystal structure.

In the title compound, the bond lengths and angles are comparable to the values in the similar Schiff bases (Zhou *et al.*, 2002). The phenanthrene ring (C1···C14) and dithiocarbazate (N1/N2/S1/S2/C15) fragments lie essentially in the same plane, with a mean deviation from the least-squares plane of 0.0385 Å. The phenanthrene ring (C1···C14) is nearly perpendicular to the phenyl ring (C17···C22) with a dihedral angle of 87.2°.

In the crystal structure, there are intramolecular N—H···O type hydrogen bonds (Table 1). The crystal structure is consolidated by intermolecular C—H···O [3.239 Å] (Fig. 2). It is also stabilized by C—H···Π interactions such as C5—H5···Π (3.642 Å) and C9—H9···Π (3.643 Å) involving phenanthrene ring and phenyl ring of the adjacent molecules respectively. In addition, π-π interactions between the adjacent phenanthrene rings (centroid-centroid distance = 3.36 (6) Å) may also stabilize the crystal packing.

S2. Experimental

S-benzyldithiocarbazate was synthesized as described in the literature (Chew *et al.*, 2004). The title compound was synthesized as described in the literature (Ali *et al.*, 2004). To 9,10-phenanthrenequinone in 60 ml of absolute ethyl alcohol was added a solution of *S*-benzyldithiocarbazate (1.00 mmol) in 20 ml of absolute ethyl alcohol dropwise. The red-brown solution was refluxed for 5.0 h at 353 K. The resultant solution was filtered and left in air for a few days, yielding brown block-like crystals.

S3. Refinement

In (I), All H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 (CH) and 0.97 Å (CH_2) and U_{iso}(H) = 1.2U_{eq}(C), and with N—H = 0.86 Å (NH) and U_{iso}(H) = 1.2U_{eq}(N).

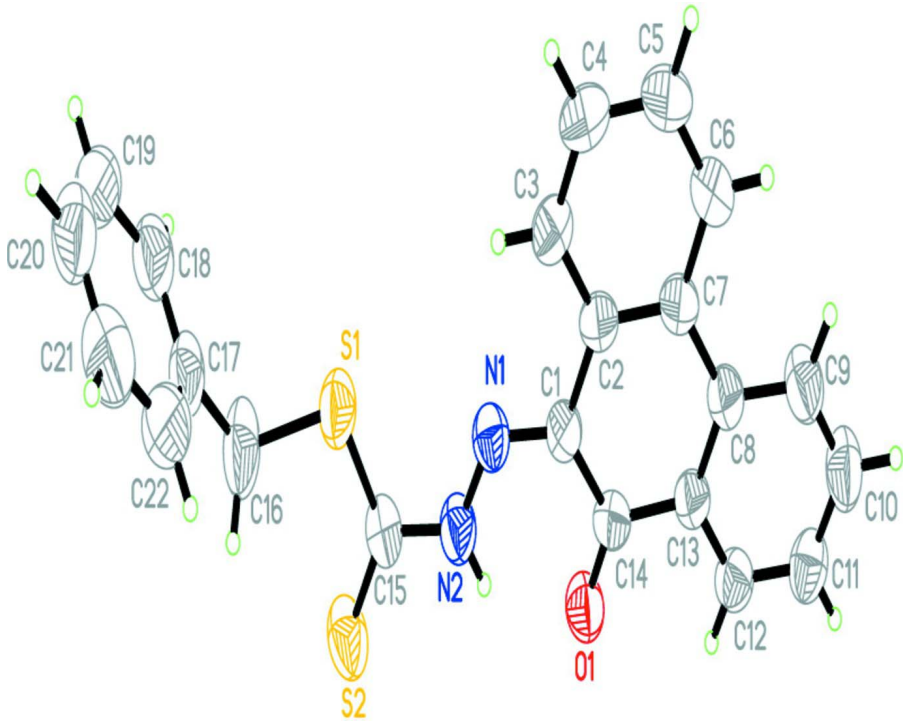

Figure 1

The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

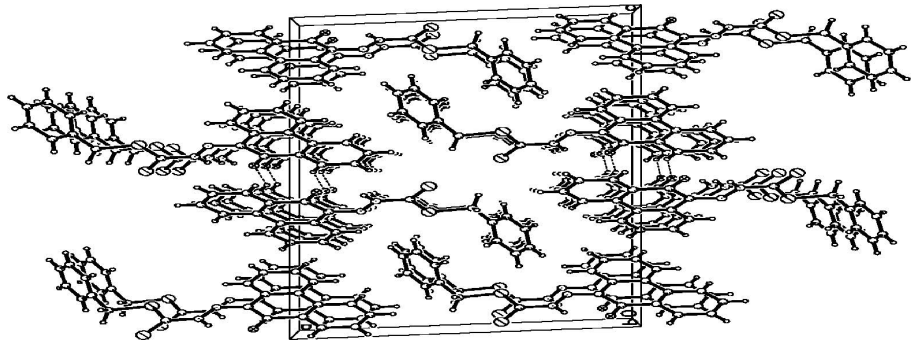

Figure 2

A view of the crystal packing along the *b* axis. Intermolecular Hydrogen bonds are shown as dashed lines.

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Crystal data

$C_{22}H_{16}N_2OS_2$
$M_r = 388.49$
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$a = 14.4945\ (19)$ Å
$b = 5.6978\ (7)$ Å
$c = 22.816\ (3)$ Å
$\beta = 93.610\ (2)°$
$V = 1880.6\ (4)$ Å^3
$Z = 4$

$F(000) = 808$
$D_x = 1.372$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3545 reflections
$\theta = 2.2–27.1°$
$\mu = 0.30$ mm^{-1}
$T = 296$ K
Block, brown
0.30 × 0.30 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.916, T_{max} = 0.943
9220 measured reflections
3316 independent reflections
2638 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.1°, θ_{min} = 2.2°
h = −17→12
k = −6→6
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.098
S = 1.06
3316 reflections
244 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
$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.4502P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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	0.12004 (12)	0.9543 (3)	0.10487 (7)	0.0410 (4)
C2	0.07744 (12)	0.7660 (3)	0.13826 (7)	0.0404 (4)
C3	0.13280 (14)	0.6058 (3)	0.17087 (8)	0.0505 (5)
H3	0.1968	0.6203	0.1718	0.061*
C4	0.09428 (15)	0.4277 (3)	0.20145 (8)	0.0570 (5)
H4	0.1320	0.3226	0.2230	0.068*
C5	−0.00057 (15)	0.4045 (3)	0.20025 (8)	0.0551 (5)
H5	−0.0269	0.2837	0.2209	0.066*
C6	−0.05593 (14)	0.5600 (3)	0.16850 (7)	0.0496 (5)
H6	−0.1198	0.5422	0.1679	0.060*
C7	−0.01904 (12)	0.7447 (3)	0.13706 (7)	0.0413 (4)
C8	−0.07862 (12)	0.9126 (3)	0.10288 (7)	0.0428 (4)
C9	−0.17451 (14)	0.8986 (4)	0.10096 (9)	0.0601 (5)
H9	−0.2023	0.7801	0.1217	0.072*
C10	−0.22943 (14)	1.0568 (4)	0.06899 (10)	0.0663 (6)
H10	−0.2934	1.0431	0.0684	0.080*

C11	−0.19058 (14)	1.2346 (4)	0.03787 (9)	0.0594 (5)
H11	−0.2279	1.3411	0.0165	0.071*
C12	−0.09620 (13)	1.2524 (3)	0.03891 (8)	0.0496 (5)
H12	−0.0693	1.3716	0.0179	0.059*
C13	−0.04017 (12)	1.0942 (3)	0.07096 (7)	0.0407 (4)
C14	0.06035 (12)	1.1237 (3)	0.07105 (7)	0.0427 (4)
C15	0.34732 (13)	1.1176 (4)	0.07602 (8)	0.0513 (5)
C16	0.51902 (14)	0.9484 (5)	0.11012 (11)	0.0836 (8)
H16A	0.5363	0.9037	0.0713	0.100*
H16B	0.5310	1.1148	0.1154	0.100*
C17	0.57478 (13)	0.8104 (4)	0.15607 (10)	0.0635 (6)
C18	0.61629 (15)	0.6028 (5)	0.14199 (11)	0.0716 (6)
H18	0.6081	0.5433	0.1041	0.086*
C19	0.67014 (17)	0.4821 (5)	0.18405 (14)	0.0816 (7)
H19	0.6984	0.3422	0.1743	0.098*
C20	0.68202 (17)	0.5671 (6)	0.23965 (13)	0.0863 (8)
H20	0.7184	0.4851	0.2677	0.104*
C21	0.64071 (19)	0.7725 (6)	0.25452 (12)	0.0867 (8)
H21	0.6489	0.8302	0.2926	0.104*
C22	0.58678 (16)	0.8938 (5)	0.21272 (12)	0.0777 (7)
H22	0.5583	1.0329	0.2229	0.093*
N1	0.20996 (10)	0.9575 (3)	0.10711 (6)	0.0466 (4)
N2	0.25374 (10)	1.1215 (3)	0.07714 (7)	0.0524 (4)
H2	0.2225	1.2296	0.0586	0.063*
O1	0.09460 (9)	1.2850 (2)	0.04354 (6)	0.0577 (4)
S1	0.39768 (3)	0.88888 (10)	0.11712 (2)	0.06204 (18)
S2	0.39996 (4)	1.31825 (12)	0.03859 (3)	0.0741 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0420 (10)	0.0423 (10)	0.0385 (9)	−0.0001 (8)	0.0004 (7)	−0.0020 (7)
C2	0.0478 (10)	0.0376 (10)	0.0356 (8)	0.0010 (8)	0.0018 (7)	−0.0025 (7)
C3	0.0527 (11)	0.0492 (11)	0.0495 (10)	0.0071 (9)	0.0025 (8)	0.0036 (9)
C4	0.0754 (15)	0.0458 (12)	0.0496 (11)	0.0112 (10)	0.0018 (10)	0.0057 (9)
C5	0.0771 (15)	0.0438 (11)	0.0445 (10)	−0.0062 (10)	0.0052 (10)	0.0042 (8)
C6	0.0570 (11)	0.0479 (11)	0.0439 (10)	−0.0082 (9)	0.0034 (8)	−0.0003 (8)
C7	0.0492 (11)	0.0387 (10)	0.0360 (8)	−0.0024 (8)	0.0016 (7)	−0.0041 (7)
C8	0.0434 (10)	0.0463 (11)	0.0386 (9)	−0.0028 (8)	0.0016 (7)	−0.0045 (8)
C9	0.0489 (12)	0.0670 (14)	0.0646 (12)	−0.0066 (10)	0.0040 (10)	0.0138 (11)
C10	0.0422 (11)	0.0809 (16)	0.0754 (14)	0.0002 (11)	0.0008 (10)	0.0102 (12)
C11	0.0511 (12)	0.0635 (13)	0.0625 (12)	0.0100 (10)	−0.0056 (9)	0.0059 (10)
C12	0.0516 (11)	0.0474 (11)	0.0491 (10)	0.0019 (9)	−0.0015 (8)	0.0040 (9)
C13	0.0439 (10)	0.0404 (10)	0.0374 (9)	−0.0004 (8)	−0.0002 (7)	−0.0031 (7)
C14	0.0489 (10)	0.0405 (10)	0.0384 (9)	−0.0010 (8)	0.0000 (7)	0.0014 (8)
C15	0.0449 (11)	0.0611 (12)	0.0479 (10)	−0.0051 (9)	0.0027 (8)	0.0007 (9)
C16	0.0429 (12)	0.112 (2)	0.0963 (17)	0.0000 (13)	0.0097 (12)	0.0408 (16)
C17	0.0373 (11)	0.0768 (16)	0.0769 (15)	−0.0056 (11)	0.0074 (10)	0.0214 (12)

C18	0.0517 (13)	0.0797 (17)	0.0837 (16)	−0.0092 (12)	0.0081 (11)	0.0086 (13)
C19	0.0622 (15)	0.0702 (16)	0.114 (2)	0.0016 (13)	0.0165 (15)	0.0235 (16)
C20	0.0586 (15)	0.099 (2)	0.100 (2)	−0.0074 (15)	−0.0065 (14)	0.0410 (18)
C21	0.0824 (18)	0.098 (2)	0.0784 (17)	−0.0195 (17)	−0.0051 (14)	0.0110 (16)
C22	0.0680 (16)	0.0705 (16)	0.0959 (19)	−0.0032 (13)	0.0151 (14)	0.0108 (14)
N1	0.0442 (9)	0.0510 (9)	0.0446 (8)	−0.0017 (7)	0.0026 (7)	0.0025 (7)
N2	0.0441 (9)	0.0563 (10)	0.0567 (9)	−0.0018 (8)	0.0021 (7)	0.0118 (8)
O1	0.0509 (8)	0.0552 (8)	0.0664 (8)	−0.0035 (7)	0.0000 (6)	0.0211 (7)
S1	0.0432 (3)	0.0684 (4)	0.0752 (4)	0.0020 (3)	0.0088 (2)	0.0171 (3)
S2	0.0586 (4)	0.0827 (4)	0.0809 (4)	−0.0146 (3)	0.0027 (3)	0.0257 (3)

Geometric parameters (Å, º)

C1—N1	1.301 (2)	C12—H12	0.9300
C1—C2	1.474 (2)	C13—C14	1.467 (2)
C1—C14	1.480 (2)	C14—O1	1.235 (2)
C2—C3	1.398 (2)	C15—N2	1.358 (2)
C2—C7	1.402 (2)	C15—S2	1.6432 (19)
C3—C4	1.370 (3)	C15—S1	1.739 (2)
C3—H3	0.9300	C16—C17	1.505 (3)
C4—C5	1.380 (3)	C16—S1	1.808 (2)
C4—H4	0.9300	C16—H16A	0.9700
C5—C6	1.371 (3)	C16—H16B	0.9700
C5—H5	0.9300	C17—C18	1.374 (3)
C6—C7	1.399 (2)	C17—C22	1.378 (3)
C6—H6	0.9300	C18—C19	1.382 (3)
C7—C8	1.478 (2)	C18—H18	0.9300
C8—C9	1.390 (3)	C19—C20	1.359 (4)
C8—C13	1.401 (2)	C19—H19	0.9300
C9—C10	1.380 (3)	C20—C21	1.367 (4)
C9—H9	0.9300	C20—H20	0.9300
C10—C11	1.378 (3)	C21—C22	1.380 (3)
C10—H10	0.9300	C21—H21	0.9300
C11—C12	1.371 (3)	C22—H22	0.9300
C11—H11	0.9300	N1—N2	1.341 (2)
C12—C13	1.390 (2)	N2—H2	0.8600
N1—C1—C2	116.18 (15)	C12—C13—C14	118.28 (16)
N1—C1—C14	124.21 (16)	C8—C13—C14	120.78 (15)
C2—C1—C14	119.60 (15)	O1—C14—C13	121.05 (16)
C3—C2—C7	119.49 (16)	O1—C14—C1	120.66 (16)
C3—C2—C1	120.34 (16)	C13—C14—C1	118.29 (15)
C7—C2—C1	120.17 (15)	N2—C15—S2	119.68 (15)
C4—C3—C2	121.05 (18)	N2—C15—S1	112.82 (14)
C4—C3—H3	119.5	S2—C15—S1	127.49 (12)
C2—C3—H3	119.5	C17—C16—S1	108.87 (15)
C3—C4—C5	119.87 (18)	C17—C16—H16A	109.9
C3—C4—H4	120.1	S1—C16—H16A	109.9

C5—C4—H4	120.1	C17—C16—H16B	109.9
C6—C5—C4	119.87 (18)	S1—C16—H16B	109.9
C6—C5—H5	120.1	H16A—C16—H16B	108.3
C4—C5—H5	120.1	C18—C17—C22	119.0 (2)
C5—C6—C7	121.82 (18)	C18—C17—C16	120.7 (2)
C5—C6—H6	119.1	C22—C17—C16	120.3 (2)
C7—C6—H6	119.1	C17—C18—C19	120.2 (2)
C6—C7—C2	117.90 (16)	C17—C18—H18	119.9
C6—C7—C8	121.88 (16)	C19—C18—H18	119.9
C2—C7—C8	120.22 (15)	C20—C19—C18	120.3 (3)
C9—C8—C13	117.11 (17)	C20—C19—H19	119.9
C9—C8—C7	121.96 (17)	C18—C19—H19	119.9
C13—C8—C7	120.92 (15)	C19—C20—C21	120.3 (3)
C10—C9—C8	121.44 (19)	C19—C20—H20	119.8
C10—C9—H9	119.3	C21—C20—H20	119.8
C8—C9—H9	119.3	C20—C21—C22	119.7 (3)
C11—C10—C9	120.78 (19)	C20—C21—H21	120.2
C11—C10—H10	119.6	C22—C21—H21	120.2
C9—C10—H10	119.6	C17—C22—C21	120.5 (3)
C12—C11—C10	119.03 (19)	C17—C22—H22	119.7
C12—C11—H11	120.5	C21—C22—H22	119.7
C10—C11—H11	120.5	C1—N1—N2	119.66 (15)
C11—C12—C13	120.71 (18)	N1—N2—C15	120.22 (16)
C11—C12—H12	119.6	N1—N2—H2	119.9
C13—C12—H12	119.6	C15—N2—H2	119.9
C12—C13—C8	120.93 (16)	C15—S1—C16	100.92 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.86	1.89	2.560 (2)	134
C12—H12···O1^{i}	0.93	2.42	3.239 (2)	147
C5—H5···*Cg*1^{ii}	0.93	2.76	3.559 (2)	144

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