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# organic compounds

# Ethyl 2-amino-4-(4-methyl-1,3-thiazol-5-yl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carboxylate

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There are two independent molecules in the asymmetric unit of the title compound, $C_{19}H_{16}N_2O_5S$, in which the thiazole rings make dihedral angles of 80.89 (11) and 84.81 (11)° with the pyrano[3,2-c]chromene ring systems. An intramolecular N—H···O hydrogen bond involving the amino group occurs in each independent molecule. In the crystal, the amino groups are involved in N—H···O and N—H···N hydrogen bonds.

## Related literature

For similar conformations were observed in the structures of ethyl 2-amino-5-oxo-4-(p-tolyl)-4H,5H-pyrano[3,2-c]chromene-8-carboxylate (Wang et al., 2004) and ethyl 2-amino-4-(2,4-dichlorophenyl)-4H-benzo[f]chromene-3-carboxylate (Shi et al., 2003). For applications of 4H-chromene and its derivatives, see: Jeso & Nicolaou (2009); Alvey et al. (2008, 2009); Bedair et al. (2001); El-Agrody et al. (2002, 2011); Abd-El-Aziz et al. (2004); Sabry et al. (2011).
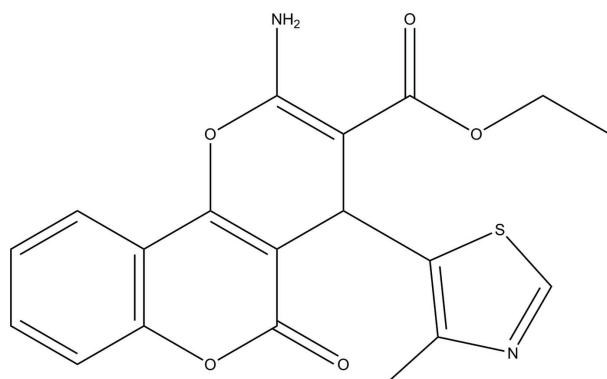


## Experimental

### Crystal data

| | |
|---|---|
| $C_{19}H_{16}N_2O_5S$ | $V = 3700.1$ (4) Å³ |
| $M_r = 384.41$ | $Z = 8$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 15.6232$ (10) Å | $\mu = 0.21$ mm⁻¹ |
| $b = 15.0696$ (9) Å | $T = 298$ K |
| $c = 15.9063$ (11) Å | $0.35 \times 0.25 \times 0.15$ mm |
| $\beta = 98.873$ (2)° | |

### Data collection

| | |
|---|---|
| Bruker APEXII CCD area-detector diffractometer | 18921 measured reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2004) | 6130 independent reflections |
| | 3527 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.931$, $T_{max} = 0.970$ | $R_{int} = 0.042$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | 491 parameters |
| $wR(F^2) = 0.145$ | H-atom parameters constrained |
| $S = 1.03$ | $\Delta\rho_{max} = 0.20$ e Å⁻³ |
| 6130 reflections | $\Delta\rho_{min} = -0.29$ e Å⁻³ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1B···O4 | 0.86 | 2.11 | 2.698 (3) | 125 |
| N1—H1B···N2Aⁱ | 0.86 | 2.49 | 3.152 (3) | 135 |
| N1—H1C···N2ⁱⁱ | 0.86 | 2.27 | 3.116 (4) | 167 |
| N1A—H1A2···N2Aⁱⁱⁱ | 0.86 | 2.13 | 2.988 (3) | 174 |
| N1A—H1A1···O4A | 0.86 | 2.09 | 2.690 (3) | 126 |
| N1A—H1A1···O4ⁱⁱ | 0.86 | 2.52 | 2.936 (3) | 111 |

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: SHELXL97.

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# supporting information

# Ethyl 2-amino-4-(4-methyl-1,3-thiazol-5-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carboxylate

**V. Karthikeyan, V. Ramkumar and R. Joel Karunakaran**

### S1. Comment

Thiazoles are important class of heterocyclic compounds, found in many potent biologically active molecules such as Sulfathiazol (antimicrobial drug), Ritonavir (antiretroviral drug) and Tiazofurin (antineoplastic drug) similarly 4-Hydroxycoumarin forms the nucleus of many natural products and drugs and is also a key intermediate for the widely used oral anticoagulants and rodenticides. There is interest in fused pyranochromenes because chromene derivatives (Jeso & Nicolaou, 2009; Alvey *et al.*, 2008, 2009); can be used as immunomodulators and for the treatment of different diseases of connective tissues, diabetes, anti-cancer and for applications of 4*H*-chromene and its derivatives, (Bedair *et al.* (2001); El-Agrody *et al.* (2002, 2011); Abd-El-Aziz *et al.* (2004); Sabry *et al.* (2011)). We present here the synthesis and crystal structure of the title compound,(I). The molecule is being assessed for biological activity. In the title compound,$C_{19}H_{16}N_2O_5$, there are two independent molecules in the asymmetric unit. The thiazole rings make a dihedral angle with 4H, 5*H*-pyrano[3,2-*c*]chromene ring system of 80.89 (11) and 84.81 (11)°. In the crystal structure, the amino groups are involved in both intra-and intermolecular N—H···O and N—H···N hydrogen bonds respectively, table1.

### S2. Experimental

A solution of heteroaromatic aldehyde (1 mmol), 1.2 mmol of alkylnitriles, 4-Hydroxy coumarins(1.1 mmol) and catalytic amount of silver trifluoromethanesulfonate (5 mol %) in 10 mL of ethanol and the reaction mixture refluxed for two hours. After completion of the reaction, which was monitored by TLC, the reaction mixture was cooled to room temperature and kept overnight in a refrigerator. The solid mass separated out was filtered and purified by column chromatography using n-Hexane: Ethylacetate mixture in the ratio (3:2). The crude product formed was recrystallized in ethanol.

### S3. Refinement

All hydrogen atoms were fixed geometrically and allowed to ride on the parent carbon atoms with aromatic C—H = 0.93 Å, methine C—H = 0.98 Å me thylene C—H = 0.97 Å and methyl C—H = 0.96 Å. The displacement parameters were set for phenyl H atoms at $U_{iso}(H) = 1.2U_{eq}(C,N)$ and for methine,methylene and methyl H atoms at $U_{iso}(H) = 1.5U_{eq}(C)$.
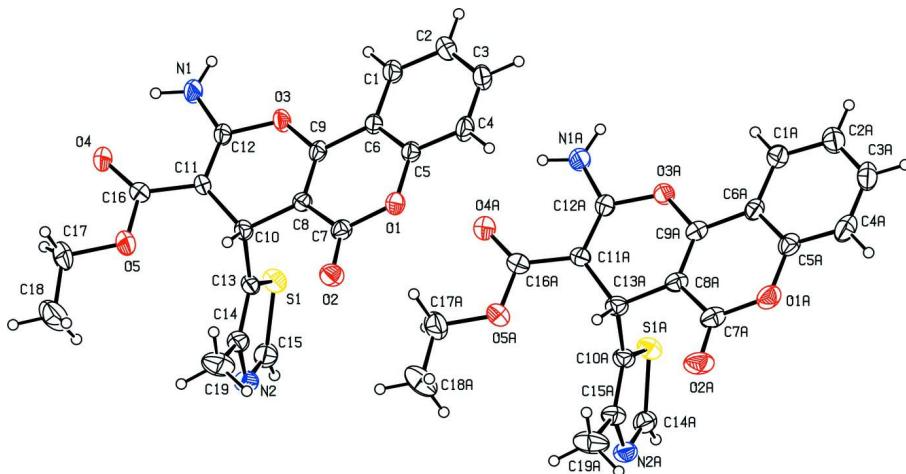
**Figure 1**

*ORTEP* of the molecule with atoms represented as 30% probability ellipsoids.

**Ethyl 2-amino-4-(4-methyl-1,3-thiazol-5-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carboxylate**

*Crystal data*

| | |
|---|---|
| $C_{19}H_{16}N_2O_5S$ | $F(000) = 1600$ |
| $M_r = 384.41$ | $D_x = 1.380$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 15.6232$ (10) Å | Cell parameters from 3286 reflections |
| $b = 15.0696$ (9) Å | $\theta = 2.4–21.4°$ |
| $c = 15.9063$ (11) Å | $\mu = 0.21$ mm$^{-1}$ |
| $\beta = 98.873$ (2)° | $T = 298$ K |
| $V = 3700.1$ (4) Å$^3$ | Rectangular, yellow |
| $Z = 8$ | $0.35 \times 0.25 \times 0.15$ mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD area-detector diffractometer | 6130 independent reflections |
| Radiation source: fine-focus sealed tube | 3527 reflections with $I > 2\sigma(I)$ |
| phi and $\omega$ scans | $R_{int} = 0.042$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2004) | $\theta_{max} = 25.0°$, $\theta_{min} = 1.9°$ |
| $T_{min} = 0.931$, $T_{max} = 0.970$ | $h = -13 \rightarrow 18$ |
| 18921 measured reflections | $k = -16 \rightarrow 14$ |
| | $l = -18 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | $w = 1/[\sigma^2(F_o^2) + (0.0714P)^2]$ |
| $wR(F^2) = 0.145$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{max} = 0.003$ |
| 6130 reflections | $\Delta\rho_{max} = 0.20$ e Å$^{-3}$ |
| 491 parameters | $\Delta\rho_{min} = -0.29$ e Å$^{-3}$ |
| 0 restraints | |

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.3585 (2) | 0.4642 (2) | 0.70875 (18) | 0.0433 (8) |
| H1 | 0.3209 | 0.4686 | 0.7485 | 0.052* |
| C2 | 0.3845 (2) | 0.5395 (2) | 0.67213 (19) | 0.0500 (9) |
| H2 | 0.3639 | 0.5946 | 0.6862 | 0.060* |
| C3 | 0.4417 (2) | 0.5334 (2) | 0.61380 (19) | 0.0510 (9) |
| H3 | 0.4599 | 0.5847 | 0.5894 | 0.061* |
| C4 | 0.4715 (2) | 0.4524 (2) | 0.59173 (18) | 0.0483 (9) |
| H4 | 0.5098 | 0.4484 | 0.5526 | 0.058* |
| C5 | 0.44379 (18) | 0.3771 (2) | 0.62839 (17) | 0.0360 (7) |
| C6 | 0.38746 (18) | 0.38107 (19) | 0.68747 (16) | 0.0332 (7) |
| C7 | 0.45393 (19) | 0.2176 (2) | 0.63881 (17) | 0.0380 (7) |
| C8 | 0.39486 (18) | 0.22000 (19) | 0.69980 (16) | 0.0334 (7) |
| C9 | 0.36581 (18) | 0.2982 (2) | 0.72308 (16) | 0.0343 (7) |
| C10 | 0.37038 (19) | 0.13370 (18) | 0.73763 (17) | 0.0357 (7) |
| H10 | 0.4235 | 0.0987 | 0.7523 | 0.043* |
| C11 | 0.33538 (19) | 0.15276 (19) | 0.81953 (17) | 0.0357 (7) |
| C12 | 0.30737 (19) | 0.2347 (2) | 0.83743 (17) | 0.0374 (7) |
| C13 | 0.30880 (19) | 0.08051 (18) | 0.67326 (17) | 0.0359 (7) |
| C14 | 0.3214 (2) | −0.0002 (2) | 0.63837 (19) | 0.0453 (8) |
| C15 | 0.1869 (3) | 0.0224 (2) | 0.5769 (2) | 0.0572 (10) |
| H15 | 0.1343 | 0.0116 | 0.5422 | 0.069* |
| C16 | 0.3354 (2) | 0.0848 (2) | 0.88338 (19) | 0.0449 (8) |
| C17 | 0.3666 (4) | −0.0665 (3) | 0.9178 (2) | 0.1105 (19) |
| H17A | 0.4128 | −0.0588 | 0.9656 | 0.133* |
| H17B | 0.3120 | −0.0676 | 0.9397 | 0.133* |
| C18 | 0.3781 (3) | −0.1472 (3) | 0.8767 (3) | 0.1049 (16) |
| H18A | 0.3376 | −0.1507 | 0.8248 | 0.157* |
| H18B | 0.3684 | −0.1957 | 0.9132 | 0.157* |
| H18C | 0.4361 | −0.1503 | 0.8639 | 0.157* |
| C19 | 0.4028 (3) | −0.0539 (2) | 0.6518 (2) | 0.0752 (12) |
| H19A | 0.4459 | −0.0238 | 0.6912 | 0.113* |
| H19B | 0.4235 | −0.0613 | 0.5985 | 0.113* |
| H19C | 0.3912 | −0.1110 | 0.6743 | 0.113* |
| C1A | 0.3840 (2) | 0.7211 (2) | 0.20315 (18) | 0.0483 (9) |
| H1A | 0.3506 | 0.7324 | 0.2456 | 0.058* |
| C2A | 0.4120 (2) | 0.7901 (2) | 0.1583 (2) | 0.0562 (9) |
| H2A | 0.3975 | 0.8481 | 0.1703 | 0.067* |
| C3A | 0.4616 (2) | 0.7739 (3) | 0.0952 (2) | 0.0599 (10) |
| H3A | 0.4804 | 0.8212 | 0.0653 | 0.072* |

| | | | |
|---|---|---|---|
| C4A | 0.4834 (2) | 0.6890 (3) | 0.07611 (19) | 0.0579 (10) |
| H4A | 0.5165 | 0.6783 | 0.0333 | 0.069* |
| C5A | 0.4555 (2) | 0.6196 (2) | 0.12157 (18) | 0.0450 (8) |
| C6A | 0.40567 (19) | 0.6337 (2) | 0.18521 (17) | 0.0395 (8) |
| C7A | 0.4552 (2) | 0.4608 (2) | 0.14276 (19) | 0.0480 (9) |
| C8A | 0.40041 (19) | 0.4741 (2) | 0.20780 (17) | 0.0392 (8) |
| C9A | 0.37984 (19) | 0.5566 (2) | 0.22772 (17) | 0.0392 (8) |
| C10A | 0.3687 (2) | 0.39270 (19) | 0.24977 (18) | 0.0415 (8) |
| H10A | 0.4182 | 0.3532 | 0.2665 | 0.050* |
| C11A | 0.33376 (19) | 0.4208 (2) | 0.32967 (17) | 0.0382 (8) |
| C12A | 0.3164 (2) | 0.5074 (2) | 0.34506 (18) | 0.0413 (8) |
| C13A | 0.30238 (19) | 0.34343 (19) | 0.18653 (18) | 0.0394 (8) |
| C14A | 0.1765 (2) | 0.2990 (2) | 0.08913 (18) | 0.0489 (9) |
| H14A | 0.1233 | 0.2933 | 0.0542 | 0.059* |
| C15A | 0.3095 (2) | 0.2642 (2) | 0.14837 (19) | 0.0449 (8) |
| C16A | 0.3177 (2) | 0.3561 (2) | 0.3915 (2) | 0.0472 (8) |
| C17A | 0.3257 (3) | 0.2039 (2) | 0.4303 (2) | 0.0780 (13) |
| H17C | 0.2641 | 0.1987 | 0.4319 | 0.094* |
| H17D | 0.3546 | 0.2182 | 0.4871 | 0.094* |
| C18A | 0.3591 (4) | 0.1201 (3) | 0.4024 (3) | 0.132 (2) |
| H18D | 0.3315 | 0.1071 | 0.3455 | 0.198* |
| H18E | 0.3471 | 0.0733 | 0.4399 | 0.198* |
| H18F | 0.4205 | 0.1248 | 0.4034 | 0.198* |
| C19A | 0.3861 (2) | 0.2038 (2) | 0.1600 (2) | 0.0764 (12) |
| H20X | 0.4044 | 0.1934 | 0.1059 | 0.115* |
| H19X | 0.3706 | 0.1484 | 0.1834 | 0.115* |
| H21X | 0.4325 | 0.2307 | 0.1981 | 0.115* |
| N1 | 0.27345 (17) | 0.26186 (17) | 0.90444 (15) | 0.0552 (8) |
| H1B | 0.2668 | 0.2250 | 0.9442 | 0.066* |
| H1C | 0.2581 | 0.3164 | 0.9082 | 0.066* |
| N2 | 0.2506 (2) | −0.03345 (19) | 0.58422 (16) | 0.0541 (7) |
| N1A | 0.28373 (18) | 0.54145 (17) | 0.40989 (15) | 0.0577 (8) |
| H1A1 | 0.2706 | 0.5073 | 0.4493 | 0.069* |
| H1A2 | 0.2756 | 0.5978 | 0.4126 | 0.069* |
| N2A | 0.23690 (18) | 0.23858 (17) | 0.09262 (15) | 0.0473 (7) |
| O1 | 0.47619 (13) | 0.29715 (14) | 0.60465 (11) | 0.0430 (5) |
| O2 | 0.48555 (14) | 0.15115 (14) | 0.61402 (13) | 0.0505 (6) |
| O3 | 0.31266 (13) | 0.30626 (12) | 0.78376 (12) | 0.0434 (5) |
| O4 | 0.31017 (17) | 0.09227 (14) | 0.95117 (14) | 0.0642 (7) |
| O5 | 0.36704 (17) | 0.00778 (15) | 0.85867 (13) | 0.0666 (7) |
| O1A | 0.47929 (14) | 0.53504 (16) | 0.10116 (12) | 0.0537 (6) |
| O2A | 0.48122 (15) | 0.39022 (17) | 0.12158 (15) | 0.0656 (7) |
| O3A | 0.33117 (14) | 0.57478 (12) | 0.29067 (12) | 0.0453 (6) |
| O4A | 0.28704 (17) | 0.36983 (14) | 0.45668 (14) | 0.0619 (7) |
| O5A | 0.34104 (15) | 0.27344 (14) | 0.37173 (13) | 0.0590 (6) |
| S1 | 0.20650 (6) | 0.11782 (6) | 0.63551 (5) | 0.0507 (3) |
| S1A | 0.20197 (5) | 0.38856 (5) | 0.15289 (5) | 0.0484 (3) |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.049 (2) | 0.042 (2) | 0.0415 (18) | −0.0003 (16) | 0.0142 (15) | 0.0060 (16) |
| C2 | 0.060 (2) | 0.037 (2) | 0.053 (2) | −0.0018 (17) | 0.0116 (18) | 0.0078 (16) |
| C3 | 0.064 (2) | 0.044 (2) | 0.0453 (19) | −0.0088 (18) | 0.0071 (17) | 0.0127 (16) |
| C4 | 0.057 (2) | 0.054 (2) | 0.0367 (18) | −0.0094 (19) | 0.0154 (16) | 0.0099 (16) |
| C5 | 0.0385 (18) | 0.038 (2) | 0.0321 (16) | −0.0052 (15) | 0.0058 (14) | 0.0017 (14) |
| C6 | 0.0364 (17) | 0.0336 (19) | 0.0297 (15) | −0.0022 (15) | 0.0054 (13) | 0.0035 (13) |
| C7 | 0.0371 (18) | 0.042 (2) | 0.0356 (17) | −0.0046 (16) | 0.0073 (14) | −0.0029 (15) |
| C8 | 0.0348 (18) | 0.0332 (19) | 0.0331 (16) | −0.0007 (14) | 0.0086 (14) | −0.0013 (13) |
| C9 | 0.0341 (18) | 0.042 (2) | 0.0287 (15) | −0.0054 (15) | 0.0091 (13) | 0.0040 (14) |
| C10 | 0.0395 (18) | 0.0319 (18) | 0.0375 (16) | −0.0021 (14) | 0.0117 (14) | 0.0029 (13) |
| C11 | 0.0462 (19) | 0.0272 (19) | 0.0343 (16) | −0.0032 (15) | 0.0087 (14) | 0.0055 (13) |
| C12 | 0.0440 (19) | 0.036 (2) | 0.0338 (16) | −0.0011 (15) | 0.0126 (14) | 0.0060 (14) |
| C13 | 0.0435 (19) | 0.0272 (18) | 0.0389 (17) | −0.0025 (14) | 0.0122 (14) | 0.0020 (13) |
| C14 | 0.054 (2) | 0.040 (2) | 0.0455 (19) | −0.0012 (17) | 0.0175 (17) | −0.0026 (15) |
| C15 | 0.064 (3) | 0.059 (3) | 0.047 (2) | −0.018 (2) | 0.0033 (18) | −0.0006 (17) |
| C16 | 0.062 (2) | 0.033 (2) | 0.0415 (19) | −0.0010 (17) | 0.0118 (17) | −0.0003 (16) |
| C17 | 0.229 (6) | 0.041 (3) | 0.066 (3) | 0.024 (3) | 0.037 (3) | 0.024 (2) |
| C18 | 0.152 (5) | 0.048 (3) | 0.103 (3) | 0.003 (3) | −0.018 (3) | 0.014 (2) |
| C19 | 0.078 (3) | 0.054 (3) | 0.097 (3) | 0.011 (2) | 0.024 (2) | −0.020 (2) |
| C1A | 0.055 (2) | 0.048 (2) | 0.0406 (18) | −0.0030 (18) | 0.0042 (16) | 0.0028 (16) |
| C2A | 0.060 (2) | 0.052 (2) | 0.053 (2) | −0.0077 (19) | −0.0011 (19) | 0.0086 (18) |
| C3A | 0.066 (3) | 0.064 (3) | 0.045 (2) | −0.020 (2) | −0.0038 (19) | 0.0170 (19) |
| C4A | 0.059 (2) | 0.080 (3) | 0.0356 (18) | −0.016 (2) | 0.0104 (16) | 0.0028 (19) |
| C5A | 0.044 (2) | 0.055 (2) | 0.0348 (17) | −0.0073 (18) | 0.0022 (15) | −0.0017 (16) |
| C6A | 0.0421 (19) | 0.047 (2) | 0.0291 (16) | −0.0042 (16) | 0.0041 (14) | 0.0013 (14) |
| C7A | 0.045 (2) | 0.057 (3) | 0.0427 (19) | −0.0045 (19) | 0.0114 (16) | −0.0123 (18) |
| C8A | 0.0362 (19) | 0.044 (2) | 0.0379 (17) | −0.0043 (15) | 0.0094 (14) | −0.0087 (15) |
| C9A | 0.0403 (19) | 0.045 (2) | 0.0329 (17) | −0.0008 (16) | 0.0064 (14) | −0.0064 (15) |
| C10A | 0.0434 (19) | 0.038 (2) | 0.0440 (18) | 0.0058 (16) | 0.0110 (15) | −0.0054 (15) |
| C11A | 0.045 (2) | 0.031 (2) | 0.0392 (17) | −0.0036 (15) | 0.0090 (15) | −0.0037 (14) |
| C12A | 0.048 (2) | 0.041 (2) | 0.0375 (18) | −0.0030 (16) | 0.0149 (15) | 0.0013 (15) |
| C13A | 0.042 (2) | 0.0343 (19) | 0.0441 (18) | 0.0028 (15) | 0.0128 (15) | −0.0048 (15) |
| C14A | 0.052 (2) | 0.053 (2) | 0.0424 (19) | −0.0091 (19) | 0.0088 (16) | −0.0053 (16) |
| C15A | 0.047 (2) | 0.039 (2) | 0.0494 (19) | 0.0021 (17) | 0.0112 (17) | −0.0092 (16) |
| C16A | 0.056 (2) | 0.037 (2) | 0.048 (2) | −0.0064 (17) | 0.0073 (17) | −0.0043 (16) |
| C17A | 0.114 (4) | 0.051 (3) | 0.060 (2) | −0.009 (2) | −0.014 (2) | 0.015 (2) |
| C18A | 0.224 (7) | 0.041 (3) | 0.134 (4) | 0.026 (3) | 0.038 (4) | 0.008 (3) |
| C19A | 0.070 (3) | 0.059 (3) | 0.097 (3) | 0.019 (2) | 0.002 (2) | −0.029 (2) |
| N1 | 0.088 (2) | 0.0408 (17) | 0.0458 (16) | 0.0083 (15) | 0.0388 (16) | 0.0078 (13) |
| N2 | 0.066 (2) | 0.0483 (19) | 0.0489 (17) | −0.0119 (17) | 0.0105 (15) | −0.0081 (14) |
| N1A | 0.090 (2) | 0.0409 (17) | 0.0509 (17) | 0.0079 (15) | 0.0370 (16) | 0.0016 (13) |
| N2A | 0.0552 (19) | 0.0448 (18) | 0.0449 (16) | −0.0033 (15) | 0.0168 (14) | −0.0096 (13) |
| O1 | 0.0501 (14) | 0.0427 (14) | 0.0400 (12) | −0.0067 (11) | 0.0194 (10) | 0.0034 (10) |
| O2 | 0.0545 (15) | 0.0446 (15) | 0.0574 (14) | 0.0001 (12) | 0.0247 (12) | −0.0051 (11) |
| O3 | 0.0574 (14) | 0.0333 (12) | 0.0454 (12) | 0.0046 (10) | 0.0272 (11) | 0.0093 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O4 | 0.110 (2) | 0.0454 (14) | 0.0434 (13) | −0.0031 (14) | 0.0307 (14) | 0.0088 (11) |
| O5 | 0.114 (2) | 0.0379 (15) | 0.0519 (14) | 0.0119 (14) | 0.0255 (14) | 0.0121 (11) |
| O1A | 0.0576 (15) | 0.0633 (17) | 0.0442 (13) | −0.0056 (13) | 0.0208 (11) | −0.0059 (12) |
| O2A | 0.0713 (18) | 0.0610 (17) | 0.0717 (16) | 0.0015 (14) | 0.0345 (14) | −0.0232 (13) |
| O3A | 0.0601 (15) | 0.0358 (13) | 0.0453 (12) | 0.0057 (11) | 0.0251 (11) | 0.0003 (10) |
| O4A | 0.0930 (19) | 0.0478 (15) | 0.0487 (14) | −0.0059 (13) | 0.0231 (13) | 0.0018 (11) |
| O5A | 0.0852 (19) | 0.0352 (15) | 0.0562 (14) | 0.0033 (13) | 0.0094 (13) | 0.0022 (11) |
| S1 | 0.0503 (6) | 0.0434 (6) | 0.0562 (5) | −0.0018 (4) | 0.0015 (4) | 0.0026 (4) |
| S1A | 0.0482 (5) | 0.0384 (5) | 0.0594 (5) | 0.0043 (4) | 0.0107 (4) | −0.0031 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.365 (4) | C1A—H1A | 0.9300 |
| C1—C6 | 1.392 (4) | C2A—C3A | 1.380 (4) |
| C1—H1 | 0.9300 | C2A—H2A | 0.9300 |
| C2—C3 | 1.387 (4) | C3A—C4A | 1.370 (5) |
| C2—H2 | 0.9300 | C3A—H3A | 0.9300 |
| C3—C4 | 1.372 (4) | C4A—C5A | 1.380 (4) |
| C3—H3 | 0.9300 | C4A—H4A | 0.9300 |
| C4—C5 | 1.375 (4) | C5A—O1A | 1.380 (4) |
| C4—H4 | 0.9300 | C5A—C6A | 1.385 (4) |
| C5—O1 | 1.382 (3) | C6A—C9A | 1.433 (4) |
| C5—C6 | 1.384 (4) | C7A—O2A | 1.205 (4) |
| C6—C9 | 1.433 (4) | C7A—O1A | 1.381 (4) |
| C7—O2 | 1.209 (3) | C7A—C8A | 1.455 (4) |
| C7—O1 | 1.383 (3) | C8A—C9A | 1.335 (4) |
| C7—C8 | 1.439 (4) | C8A—C10A | 1.516 (4) |
| C8—C9 | 1.336 (4) | C9A—O3A | 1.375 (3) |
| C8—C10 | 1.507 (4) | C10A—C11A | 1.518 (4) |
| C9—O3 | 1.372 (3) | C10A—C13A | 1.521 (4) |
| C10—C11 | 1.516 (4) | C10A—H10A | 0.9800 |
| C10—C13 | 1.521 (4) | C11A—C12A | 1.363 (4) |
| C10—H10 | 0.9800 | C11A—C16A | 1.434 (4) |
| C11—C12 | 1.355 (4) | C12A—N1A | 1.323 (3) |
| C11—C16 | 1.442 (4) | C12A—O3A | 1.376 (3) |
| C12—N1 | 1.326 (3) | C13A—C15A | 1.352 (4) |
| C12—O3 | 1.385 (3) | C13A—S1A | 1.718 (3) |
| C13—C14 | 1.364 (4) | C14A—N2A | 1.305 (4) |
| C13—S1 | 1.713 (3) | C14A—S1A | 1.699 (3) |
| C14—N2 | 1.387 (4) | C14A—H14A | 0.9300 |
| C14—C19 | 1.494 (5) | C15A—N2A | 1.382 (4) |
| C15—N2 | 1.294 (4) | C15A—C19A | 1.492 (4) |
| C15—S1 | 1.715 (3) | C16A—O4A | 1.225 (3) |
| C15—H15 | 0.9300 | C16A—O5A | 1.349 (4) |
| C16—O4 | 1.209 (3) | C17A—O5A | 1.446 (4) |
| C16—O5 | 1.344 (4) | C17A—C18A | 1.461 (5) |
| C17—C18 | 1.406 (5) | C17A—H17C | 0.9700 |
| C17—O5 | 1.463 (4) | C17A—H17D | 0.9700 |

| | | | |
|---|---|---|---|
| C17—H17A | 0.9700 | C18A—H18D | 0.9600 |
| C17—H17B | 0.9700 | C18A—H18E | 0.9600 |
| C18—H18A | 0.9600 | C18A—H18F | 0.9600 |
| C18—H18B | 0.9600 | C19A—H20X | 0.9600 |
| C18—H18C | 0.9600 | C19A—H19X | 0.9600 |
| C19—H19A | 0.9600 | C19A—H21X | 0.9600 |
| C19—H19B | 0.9600 | N1—H1B | 0.8600 |
| C19—H19C | 0.9600 | N1—H1C | 0.8600 |
| C1A—C2A | 1.371 (4) | N1A—H1A1 | 0.8600 |
| C1A—C6A | 1.401 (4) | N1A—H1A2 | 0.8600 |
| | | | |
| C2—C1—C6 | 121.0 (3) | C2A—C3A—H3A | 119.5 |
| C2—C1—H1 | 119.5 | C3A—C4A—C5A | 118.8 (3) |
| C6—C1—H1 | 119.5 | C3A—C4A—H4A | 120.6 |
| C1—C2—C3 | 119.7 (3) | C5A—C4A—H4A | 120.6 |
| C1—C2—H2 | 120.2 | O1A—C5A—C4A | 117.2 (3) |
| C3—C2—H2 | 120.2 | O1A—C5A—C6A | 121.1 (3) |
| C4—C3—C2 | 120.6 (3) | C4A—C5A—C6A | 121.7 (3) |
| C4—C3—H3 | 119.7 | C5A—C6A—C1A | 118.3 (3) |
| C2—C3—H3 | 119.7 | C5A—C6A—C9A | 116.8 (3) |
| C3—C4—C5 | 118.9 (3) | C1A—C6A—C9A | 124.9 (3) |
| C3—C4—H4 | 120.5 | O2A—C7A—O1A | 116.9 (3) |
| C5—C4—H4 | 120.5 | O2A—C7A—C8A | 125.5 (3) |
| C4—C5—O1 | 116.8 (3) | O1A—C7A—C8A | 117.6 (3) |
| C4—C5—C6 | 121.8 (3) | C9A—C8A—C7A | 119.1 (3) |
| O1—C5—C6 | 121.4 (3) | C9A—C8A—C10A | 122.8 (3) |
| C5—C6—C1 | 117.9 (3) | C7A—C8A—C10A | 118.1 (3) |
| C5—C6—C9 | 116.4 (3) | C8A—C9A—O3A | 122.6 (3) |
| C1—C6—C9 | 125.7 (3) | C8A—C9A—C6A | 123.2 (3) |
| O2—C7—O1 | 116.7 (3) | O3A—C9A—C6A | 114.2 (3) |
| O2—C7—C8 | 125.3 (3) | C8A—C10A—C11A | 109.1 (2) |
| O1—C7—C8 | 118.0 (3) | C8A—C10A—C13A | 109.8 (2) |
| C9—C8—C7 | 119.3 (3) | C11A—C10A—C13A | 113.2 (2) |
| C9—C8—C10 | 122.2 (2) | C8A—C10A—H10A | 108.2 |
| C7—C8—C10 | 118.4 (3) | C11A—C10A—H10A | 108.2 |
| C8—C9—O3 | 122.8 (2) | C13A—C10A—H10A | 108.2 |
| C8—C9—C6 | 123.2 (2) | C12A—C11A—C16A | 117.8 (3) |
| O3—C9—C6 | 114.0 (2) | C12A—C11A—C10A | 121.6 (3) |
| C8—C10—C11 | 109.1 (2) | C16A—C11A—C10A | 120.5 (3) |
| C8—C10—C13 | 111.1 (2) | N1A—C12A—C11A | 128.5 (3) |
| C11—C10—C13 | 113.8 (2) | N1A—C12A—O3A | 109.0 (3) |
| C8—C10—H10 | 107.5 | C11A—C12A—O3A | 122.4 (2) |
| C11—C10—H10 | 107.5 | C15A—C13A—C10A | 129.3 (3) |
| C13—C10—H10 | 107.5 | C15A—C13A—S1A | 110.1 (2) |
| C12—C11—C16 | 117.6 (3) | C10A—C13A—S1A | 120.6 (2) |
| C12—C11—C10 | 121.6 (2) | N2A—C14A—S1A | 115.3 (3) |
| C16—C11—C10 | 120.7 (3) | N2A—C14A—H14A | 122.3 |
| N1—C12—C11 | 129.2 (3) | S1A—C14A—H14A | 122.3 |

| | | | |
|---|---|---|---|
| N1—C12—O3 | 108.9 (3) | C13A—C15A—N2A | 114.7 (3) |
| C11—C12—O3 | 121.9 (2) | C13A—C15A—C19A | 127.1 (3) |
| C14—C13—C10 | 128.9 (3) | N2A—C15A—C19A | 118.2 (3) |
| C14—C13—S1 | 109.6 (2) | O4A—C16A—O5A | 120.5 (3) |
| C10—C13—S1 | 121.5 (2) | O4A—C16A—C11A | 126.8 (3) |
| C13—C14—N2 | 115.1 (3) | O5A—C16A—C11A | 112.7 (3) |
| C13—C14—C19 | 126.7 (3) | O5A—C17A—C18A | 109.2 (3) |
| N2—C14—C19 | 118.2 (3) | O5A—C17A—H17C | 109.8 |
| N2—C15—S1 | 115.2 (3) | C18A—C17A—H17C | 109.8 |
| N2—C15—H15 | 122.4 | O5A—C17A—H17D | 109.8 |
| S1—C15—H15 | 122.4 | C18A—C17A—H17D | 109.8 |
| O4—C16—O5 | 121.7 (3) | H17C—C17A—H17D | 108.3 |
| O4—C16—C11 | 126.7 (3) | C17A—C18A—H18D | 109.5 |
| O5—C16—C11 | 111.5 (3) | C17A—C18A—H18E | 109.5 |
| C18—C17—O5 | 110.4 (3) | H18D—C18A—H18E | 109.5 |
| C18—C17—H17A | 109.6 | C17A—C18A—H18F | 109.5 |
| O5—C17—H17A | 109.6 | H18D—C18A—H18F | 109.5 |
| C18—C17—H17B | 109.6 | H18E—C18A—H18F | 109.5 |
| O5—C17—H17B | 109.6 | C15A—C19A—H20X | 109.5 |
| H17A—C17—H17B | 108.1 | C15A—C19A—H19X | 109.5 |
| C17—C18—H18A | 109.5 | H20X—C19A—H19X | 109.5 |
| C17—C18—H18B | 109.5 | C15A—C19A—H21X | 109.5 |
| H18A—C18—H18B | 109.5 | H20X—C19A—H21X | 109.5 |
| C17—C18—H18C | 109.5 | H19X—C19A—H21X | 109.5 |
| H18A—C18—H18C | 109.5 | C12—N1—H1B | 120.0 |
| H18B—C18—H18C | 109.5 | C12—N1—H1C | 120.0 |
| C14—C19—H19A | 109.5 | H1B—N1—H1C | 120.0 |
| C14—C19—H19B | 109.5 | C15—N2—C14 | 110.4 (3) |
| H19A—C19—H19B | 109.5 | C12A—N1A—H1A1 | 120.0 |
| C14—C19—H19C | 109.5 | C12A—N1A—H1A2 | 120.0 |
| H19A—C19—H19C | 109.5 | H1A1—N1A—H1A2 | 120.0 |
| H19B—C19—H19C | 109.5 | C14A—N2A—C15A | 110.4 (3) |
| C2A—C1A—C6A | 120.0 (3) | C5—O1—C7 | 121.6 (2) |
| C2A—C1A—H1A | 120.0 | C9—O3—C12 | 117.7 (2) |
| C6A—C1A—H1A | 120.0 | C16—O5—C17 | 115.7 (3) |
| C1A—C2A—C3A | 120.2 (3) | C5A—O1A—C7A | 122.1 (2) |
| C1A—C2A—H2A | 119.9 | C9A—O3A—C12A | 118.4 (2) |
| C3A—C2A—H2A | 119.9 | C16A—O5A—C17A | 116.2 (3) |
| C4A—C3A—C2A | 121.0 (3) | C13—S1—C15 | 89.65 (17) |
| C4A—C3A—H3A | 119.5 | C14A—S1A—C13A | 89.39 (16) |
| | | | |
| C6—C1—C2—C3 | −1.0 (5) | C7A—C8A—C9A—C6A | 3.1 (5) |
| C1—C2—C3—C4 | 0.8 (5) | C10A—C8A—C9A—C6A | −176.5 (3) |
| C2—C3—C4—C5 | 0.0 (5) | C5A—C6A—C9A—C8A | −1.0 (5) |
| C3—C4—C5—O1 | −179.5 (3) | C1A—C6A—C9A—C8A | 178.7 (3) |
| C3—C4—C5—C6 | −0.7 (5) | C5A—C6A—C9A—O3A | 179.5 (3) |
| C4—C5—C6—C1 | 0.5 (4) | C1A—C6A—C9A—O3A | −0.8 (4) |
| O1—C5—C6—C1 | 179.3 (2) | C9A—C8A—C10A—C11A | −15.1 (4) |

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|---|---|---|---|
| C4—C5—C6—C9 | −178.0 (3) | C7A—C8A—C10A—C11A | 165.2 (3) |
| O1—C5—C6—C9 | 0.8 (4) | C9A—C8A—C10A—C13A | 109.5 (3) |
| C2—C1—C6—C5 | 0.3 (5) | C7A—C8A—C10A—C13A | −70.2 (3) |
| C2—C1—C6—C9 | 178.7 (3) | C8A—C10A—C11A—C12A | 14.3 (4) |
| O2—C7—C8—C9 | 178.7 (3) | C13A—C10A—C11A—C12A | −108.3 (3) |
| O1—C7—C8—C9 | −2.0 (4) | C8A—C10A—C11A—C16A | −165.9 (3) |
| O2—C7—C8—C10 | 0.9 (5) | C13A—C10A—C11A—C16A | 71.4 (4) |
| O1—C7—C8—C10 | −179.8 (2) | C16A—C11A—C12A—N1A | −1.9 (5) |
| C7—C8—C9—O3 | −176.8 (2) | C10A—C11A—C12A—N1A | 177.8 (3) |
| C10—C8—C9—O3 | 0.9 (4) | C16A—C11A—C12A—O3A | 178.7 (3) |
| C7—C8—C9—C6 | 2.9 (4) | C10A—C11A—C12A—O3A | −1.6 (5) |
| C10—C8—C9—C6 | −179.4 (3) | C8A—C10A—C13A—C15A | 109.8 (3) |
| C5—C6—C9—C8 | −2.3 (4) | C11A—C10A—C13A—C15A | −128.0 (3) |
| C1—C6—C9—C8 | 179.4 (3) | C8A—C10A—C13A—S1A | −69.4 (3) |
| C5—C6—C9—O3 | 177.5 (2) | C11A—C10A—C13A—S1A | 52.8 (3) |
| C1—C6—C9—O3 | −0.9 (4) | C10A—C13A—C15A—N2A | −179.1 (3) |
| C9—C8—C10—C11 | −17.5 (4) | S1A—C13A—C15A—N2A | 0.2 (3) |
| C7—C8—C10—C11 | 160.3 (3) | C10A—C13A—C15A—C19A | 0.6 (5) |
| C9—C8—C10—C13 | 108.7 (3) | S1A—C13A—C15A—C19A | 179.9 (3) |
| C7—C8—C10—C13 | −73.5 (3) | C12A—C11A—C16A—O4A | 2.4 (5) |
| C8—C10—C11—C12 | 18.3 (4) | C10A—C11A—C16A—O4A | −177.4 (3) |
| C13—C10—C11—C12 | −106.3 (3) | C12A—C11A—C16A—O5A | −177.0 (3) |
| C8—C10—C11—C16 | −158.2 (3) | C10A—C11A—C16A—O5A | 3.3 (4) |
| C13—C10—C11—C16 | 77.2 (3) | S1—C15—N2—C14 | −1.1 (3) |
| C16—C11—C12—N1 | −5.1 (5) | C13—C14—N2—C15 | 1.7 (4) |
| C10—C11—C12—N1 | 178.3 (3) | C19—C14—N2—C15 | −177.3 (3) |
| C16—C11—C12—O3 | 173.7 (3) | S1A—C14A—N2A—C15A | −0.9 (3) |
| C10—C11—C12—O3 | −2.9 (4) | C13A—C15A—N2A—C14A | 0.4 (4) |
| C8—C10—C13—C14 | 116.2 (3) | C19A—C15A—N2A—C14A | −179.2 (3) |
| C11—C10—C13—C14 | −120.3 (3) | C4—C5—O1—C7 | 178.8 (3) |
| C8—C10—C13—S1 | −65.5 (3) | C6—C5—O1—C7 | −0.1 (4) |
| C11—C10—C13—S1 | 58.1 (3) | O2—C7—O1—C5 | 180.0 (3) |
| C10—C13—C14—N2 | 176.9 (3) | C8—C7—O1—C5 | 0.6 (4) |
| S1—C13—C14—N2 | −1.6 (3) | C8—C9—O3—C12 | 16.9 (4) |
| C10—C13—C14—C19 | −4.1 (5) | C6—C9—O3—C12 | −162.8 (2) |
| S1—C13—C14—C19 | 177.4 (3) | N1—C12—O3—C9 | 163.3 (2) |
| C12—C11—C16—O4 | 2.6 (5) | C11—C12—O3—C9 | −15.8 (4) |
| C10—C11—C16—O4 | 179.2 (3) | O4—C16—O5—C17 | 1.7 (5) |
| C12—C11—C16—O5 | −178.1 (3) | C11—C16—O5—C17 | −177.7 (3) |
| C10—C11—C16—O5 | −1.5 (4) | C18—C17—O5—C16 | 163.9 (4) |
| C6A—C1A—C2A—C3A | 0.0 (5) | C4A—C5A—O1A—C7A | 179.7 (3) |
| C1A—C2A—C3A—C4A | 0.2 (5) | C6A—C5A—O1A—C7A | −0.2 (4) |
| C2A—C3A—C4A—C5A | −0.5 (5) | O2A—C7A—O1A—C5A | −178.2 (3) |
| C3A—C4A—C5A—O1A | −179.5 (3) | C8A—C7A—O1A—C5A | 2.3 (4) |
| C3A—C4A—C5A—C6A | 0.5 (5) | C8A—C9A—O3A—C12A | 12.0 (4) |
| O1A—C5A—C6A—C1A | 179.7 (3) | C6A—C9A—O3A—C12A | −168.6 (2) |
| C4A—C5A—C6A—C1A | −0.2 (5) | N1A—C12A—O3A—C9A | 167.9 (3) |
| O1A—C5A—C6A—C9A | −0.5 (4) | C11A—C12A—O3A—C9A | −12.6 (4) |

| | | | | |
|---|---|---|---|---|
| C4A—C5A—C6A—C9A | 179.6 (3) | O4A—C16A—O5A—C17A | 1.5 (5) |
| C2A—C1A—C6A—C5A | −0.1 (5) | C11A—C16A—O5A—C17A | −179.1 (3) |
| C2A—C1A—C6A—C9A | −179.8 (3) | C18A—C17A—O5A—C16A | −176.8 (4) |
| O2A—C7A—C8A—C9A | 176.8 (3) | C14—C13—S1—C15 | 0.8 (2) |
| O1A—C7A—C8A—C9A | −3.7 (4) | C10—C13—S1—C15 | −177.8 (2) |
| O2A—C7A—C8A—C10A | −3.5 (5) | N2—C15—S1—C13 | 0.2 (3) |
| O1A—C7A—C8A—C10A | 176.0 (2) | N2A—C14A—S1A—C13A | 0.9 (2) |
| C7A—C8A—C9A—O3A | −177.4 (3) | C15A—C13A—S1A—C14A | −0.6 (2) |
| C10A—C8A—C9A—O3A | 2.9 (5) | C10A—C13A—S1A—C14A | 178.8 (2) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*B*···O4 | 0.86 | 2.11 | 2.698 (3) | 125 |
| N1—H1*B*···N2*A*[i] | 0.86 | 2.49 | 3.152 (3) | 135 |
| N1—H1*C*···N2[ii] | 0.86 | 2.27 | 3.116 (4) | 167 |
| N1*A*—H1*A*2···N2*A*[iii] | 0.86 | 2.13 | 2.988 (4) | 174 |
| N1*A*—H1*A*1···O4*A* | 0.86 | 2.09 | 2.690 (3) | 126 |
| N1*A*—H1*A*1···O4[ii] | 0.86 | 2.52 | 2.936 (3) | 111 |

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