# 4-(4-Bromophenyl)-1-(2,6-difluorobenzyl)-3-(3,4,5-trimethoxyphenyl)-1H-1,2,4-triazole-5(4H)-thione

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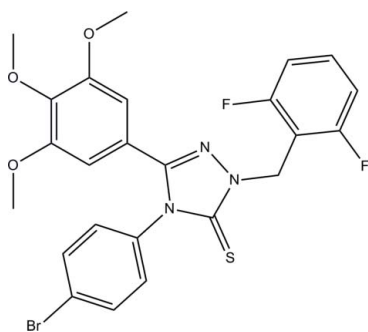Correspondence e-mail: hkfun@usm.my

In the title compound, $C_{24}H_{20}BrF_2N_3O_3S$, the triazole ring (r.m.s. deviation = 0.0107 Å) makes dihedral angles of 28.18 (14), 63.76 (14) and 77.01 (18)°, respectively, with the trimethoxy-, bromo-, and difluoro-substituted benzene rings. The C atoms of the *meta* methoxy groups are roughly coplanar with their ring [displacements = −0.289 (4) and 0.083 (7) Å], whereas the C atom of the *para* group is displaced [1.117 (3) Å]. In the crystal, inversion dimers linked by two pairs of C—H···O hydrogen bonds occur. The ring motif of the two hydrogen bonds to their symmetry-generated O-atom acceptors is $R_2^2(8)$.

## Related literature

For a related structure and background to 1,2,4-triazole derivatives, see: Fun *et al.* (2011). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



## Experimental

### Crystal data

| | |
|---|---|
| $C_{24}H_{20}BrF_2N_3O_3S$ | $V$ = 4836.4 (9) Å$^3$ |
| $M_r$ = 548.40 | $Z$ = 8 |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a$ = 17.6694 (18) Å | $\mu$ = 1.83 mm$^{-1}$ |
| $b$ = 15.5299 (16) Å | $T$ = 296 K |
| $c$ = 18.0855 (19) Å | 0.63 × 0.34 × 0.21 mm |
| $\beta$ = 102.955 (2)° | |

### Data collection

| | |
|---|---|
| Bruker APEX DUO CCD diffractometer | 20567 measured reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2009) | 7051 independent reflections |
| | 3435 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.391, $T_{max}$ = 0.703 | $R_{int}$ = 0.041 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.048 | 310 parameters |
| $wR(F^2)$ = 0.158 | H-atom parameters constrained |
| $S$ = 1.00 | $\Delta\rho_{max}$ = 0.30 e Å$^{-3}$ |
| 7051 reflections | $\Delta\rho_{min}$ = −0.44 e Å$^{-3}$ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C13—H13A···O1[i] | 0.93 | 2.54 | 3.284 (3) | 137 |
| C14—H14A···O2[i] | 0.93 | 2.40 | 3.142 (3) | 137 |

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

## References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2009). *SADABS, APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

[‡] Thomson Reuters ResearcherID: A-3561-2009.

**supplementary materials**

## 4-(4-Bromophenyl)-1-(2,6-difluorobenzyl)-3-(3,4,5-trimethoxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

### H.-K. Fun, C. W. Ooi, B. Chandrakantha, A. M. Isloor and P. Shetty

### Comment

As part of our ongoing studies of 1,2,4-triazole derivatives (Fun *et al.*, 2011), we now describe the structure of the title compound, (I).

In the title compound (Fig. 1), the triazole (N1–N3/C7/C8) ring is essentially planar with maximum deviation of 0.015 (3) Å at atom C8. The central triazole ring makes dihedral angles of 28.18 (14)°, 63.76 (14)° and 77.01 (18)° respectively with the methoxy (C1–C6), bromo (C9–C14), and difluoro (C16–C21) substituted phenyl rings. The bond lengths are comparable to a related structure (Fun *et al.*, 2011).

In the crystal (Fig. 2), the intermolecular C13—H13A···O1 and C14—H14A···O2 hydrogen bonds (Table 1) link the molecules to form $R_2^2$ (8) ring motifs (Bernstein *et al.*, 1995), leading to the formation of dimers.

### Experimental

To a solution of 4-(4-bromophenyl)-5-(3,4,5-trimethoxyphenyl)-4*H*-1,2,4- triazole-3-thiol (1 g, 0.0023 mol) in dry acetonitrile (20 ml) was added potassium carbonate (0.65 g, 0.0047 mol) followed by 2,6-difluorobenzyl bromide (0.52 g, 0.0025 mol) at room temperature. After the addition, the reaction mixture was stirred at room temperature for 6 hr. Progress of reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was concentrated and purified by column chromatography using pet ether, ethyl acetate as an eluent to afford title compound as a colourless solid. Yield 1.1 g, 85%. *M*.p: 448–453 K.

### Refinement

All the H atoms were positioned geometrically and refined using a riding model with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$ (C—H = 0.93, 0.96 or 0.97 Å). A rotating group model was applied to the methyl group. In the final refinement, one outliner (-2 0 8) was omitted.
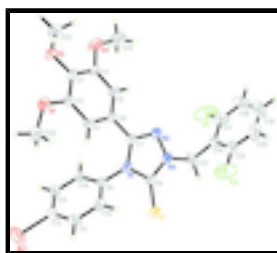
### Figures



Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids.
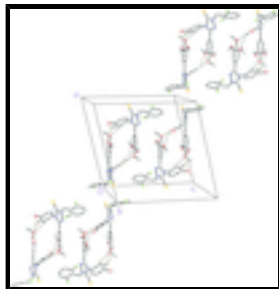
Fig. 2. The crystal packing of the title compound, viewed down *b* axis. Dashed lines represent hydrogen bonds.

**4-(4-Bromophenyl)-1-(2,6-difluorobenzyl)-3-(3,4,5-trimethoxyphenyl)-1*H*- 1,2,4-triazole-5(4*H*)-thione**

*Crystal data*

| | |
|---|---|
| $C_{24}H_{20}BrF_2N_3O_3S$ | $F(000) = 2224$ |
| $M_r = 548.40$ | $D_x = 1.506$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2yc | Cell parameters from 3384 reflections |
| $a = 17.6694$ (18) Å | $\theta = 2.3–22.8°$ |
| $b = 15.5299$ (16) Å | $\mu = 1.83$ mm$^{-1}$ |
| $c = 18.0855$ (19) Å | $T = 296$ K |
| $\beta = 102.955$ (2)° | Block, colourless |
| $V = 4836.4$ (9) Å$^3$ | $0.63 \times 0.34 \times 0.21$ mm |
| $Z = 8$ | |

*Data collection*

| | |
|---|---|
| Bruker APEX DUO CCD diffractometer | 7051 independent reflections |
| Radiation source: fine-focus sealed tube | 3435 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.041$ |
| $\varphi$ and $\omega$ scans | $\theta_{max} = 30.1°$, $\theta_{min} = 1.8°$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2009) | $h = -23 \rightarrow 24$ |
| $T_{min} = 0.391$, $T_{max} = 0.703$ | $k = -21 \rightarrow 20$ |
| 20567 measured reflections | $l = -25 \rightarrow 25$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.158$ | H-atom parameters constrained |
| $S = 1.00$ | $w = 1/[\sigma^2(F_o^2) + (0.0774P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 7051 reflections | $(\Delta/\sigma)_{max} < 0.001$ |

310 parameters

$\Delta\rho_{max} = 0.30$ e Å$^{-3}$

0 restraints

$\Delta\rho_{min} = -0.44$ 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 (Å$^2$)*

|  | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.20988 (3) | 0.55993 (2) | 0.21898 (3) | 0.1130 (2) |
| S1 | 0.42133 (3) | 0.87749 (5) | 0.42274 (5) | 0.0673 (2) |
| F1 | 0.32718 (17) | 1.22282 (19) | 0.4955 (2) | 0.1545 (12) |
| F2 | 0.42211 (15) | 0.98693 (17) | 0.64170 (17) | 0.1319 (10) |
| O1 | −0.02973 (10) | 0.76975 (11) | 0.37056 (14) | 0.0706 (6) |
| O2 | −0.11356 (9) | 0.91409 (13) | 0.34642 (12) | 0.0649 (5) |
| O3 | −0.04768 (11) | 1.06802 (12) | 0.37062 (18) | 0.0906 (8) |
| N1 | 0.26407 (10) | 0.88186 (13) | 0.41197 (11) | 0.0444 (5) |
| N2 | 0.24694 (11) | 1.00640 (14) | 0.46509 (13) | 0.0564 (6) |
| N3 | 0.32475 (11) | 0.99013 (14) | 0.46984 (13) | 0.0557 (6) |
| C1 | 0.09112 (12) | 0.85034 (16) | 0.40263 (15) | 0.0498 (6) |
| H1A | 0.1210 | 0.8005 | 0.4104 | 0.060* |
| C2 | 0.01028 (13) | 0.84511 (16) | 0.38229 (15) | 0.0520 (6) |
| C3 | −0.03423 (13) | 0.91950 (17) | 0.37176 (16) | 0.0536 (6) |
| C4 | 0.00131 (13) | 0.99918 (17) | 0.38142 (18) | 0.0609 (7) |
| C5 | 0.08213 (14) | 1.00515 (17) | 0.40030 (18) | 0.0599 (7) |
| H5A | 0.1062 | 1.0588 | 0.4056 | 0.072* |
| C6 | 0.12633 (13) | 0.93048 (15) | 0.41108 (15) | 0.0492 (6) |
| C7 | 0.21156 (13) | 0.94011 (15) | 0.43001 (15) | 0.0487 (6) |
| C8 | 0.33770 (12) | 0.91620 (17) | 0.43633 (14) | 0.0493 (6) |
| C9 | 0.24939 (12) | 0.80534 (15) | 0.36716 (13) | 0.0428 (5) |
| C10 | 0.27705 (15) | 0.72710 (18) | 0.39855 (16) | 0.0595 (7) |
| H10A | 0.3036 | 0.7241 | 0.4491 | 0.071* |
| C11 | 0.26513 (18) | 0.65378 (18) | 0.35485 (18) | 0.0694 (8) |
| H11A | 0.2838 | 0.6010 | 0.3754 | 0.083* |
| C12 | 0.22515 (15) | 0.65947 (17) | 0.28023 (16) | 0.0577 (7) |
| C13 | 0.19658 (14) | 0.73658 (17) | 0.24914 (15) | 0.0544 (6) |
| H13A | 0.1687 | 0.7391 | 0.1991 | 0.065* |
| C14 | 0.20950 (13) | 0.81059 (15) | 0.29267 (13) | 0.0468 (6) |
| H14A | 0.1914 | 0.8634 | 0.2718 | 0.056* |

| | | | | |
|---|---|---|---|---|
| C15 | 0.38362 (16) | 1.0561 (2) | 0.49590 (19) | 0.0726 (9) |
| H15A | 0.3819 | 1.0975 | 0.4554 | 0.087* |
| H15B | 0.4344 | 1.0292 | 0.5063 | 0.087* |
| C16 | 0.37404 (13) | 1.10289 (16) | 0.56521 (15) | 0.0505 (6) |
| C17 | 0.34767 (18) | 1.1854 (2) | 0.5644 (2) | 0.0794 (10) |
| C18 | 0.3428 (3) | 1.2317 (3) | 0.6272 (5) | 0.125 (2) |
| H18A | 0.3239 | 1.2878 | 0.6236 | 0.149* |
| C19 | 0.3670 (3) | 1.1915 (4) | 0.6960 (4) | 0.130 (2) |
| H19A | 0.3644 | 1.2215 | 0.7399 | 0.156* |
| C20 | 0.3937 (2) | 1.1119 (4) | 0.7023 (2) | 0.1091 (15) |
| H20A | 0.4101 | 1.0860 | 0.7495 | 0.131* |
| C21 | 0.39669 (18) | 1.0688 (2) | 0.6371 (2) | 0.0739 (9) |
| C22 | 0.01256 (18) | 0.69298 (18) | 0.3665 (2) | 0.0775 (9) |
| H22A | −0.0230 | 0.6465 | 0.3499 | 0.116* |
| H22B | 0.0441 | 0.6799 | 0.4158 | 0.116* |
| H22C | 0.0453 | 0.7006 | 0.3312 | 0.116* |
| C23 | −0.15565 (16) | 0.9151 (2) | 0.4041 (2) | 0.0742 (8) |
| H23A | −0.2103 | 0.9147 | 0.3816 | 0.111* |
| H23B | −0.1428 | 0.9661 | 0.4343 | 0.111* |
| H23C | −0.1425 | 0.8652 | 0.4357 | 0.111* |
| C24 | −0.0154 (2) | 1.1508 (2) | 0.3820 (4) | 0.1291 (19) |
| H24A | −0.0563 | 1.1929 | 0.3738 | 0.194* |
| H24B | 0.0173 | 1.1606 | 0.3470 | 0.194* |
| H24C | 0.0148 | 1.1557 | 0.4330 | 0.194* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.1658 (5) | 0.0668 (2) | 0.0968 (3) | 0.0079 (2) | 0.0091 (3) | −0.0314 (2) |
| S1 | 0.0325 (3) | 0.0908 (5) | 0.0767 (5) | 0.0032 (3) | 0.0079 (3) | −0.0227 (4) |
| F1 | 0.127 (2) | 0.136 (2) | 0.212 (3) | 0.0421 (17) | 0.065 (2) | 0.094 (2) |
| F2 | 0.130 (2) | 0.1086 (17) | 0.160 (2) | 0.0429 (15) | 0.0390 (18) | 0.0481 (17) |
| O1 | 0.0405 (9) | 0.0573 (11) | 0.1115 (17) | −0.0094 (8) | 0.0114 (10) | −0.0154 (11) |
| O2 | 0.0308 (8) | 0.0846 (12) | 0.0747 (13) | −0.0053 (8) | 0.0021 (8) | −0.0160 (11) |
| O3 | 0.0420 (10) | 0.0622 (13) | 0.159 (2) | 0.0074 (9) | 0.0055 (13) | −0.0095 (13) |
| N1 | 0.0295 (8) | 0.0537 (11) | 0.0469 (11) | −0.0002 (8) | 0.0022 (8) | −0.0066 (9) |
| N2 | 0.0328 (9) | 0.0679 (13) | 0.0687 (14) | −0.0089 (9) | 0.0119 (10) | −0.0213 (11) |
| N3 | 0.0308 (9) | 0.0750 (14) | 0.0608 (13) | −0.0074 (9) | 0.0094 (9) | −0.0233 (12) |
| C1 | 0.0336 (11) | 0.0548 (14) | 0.0599 (16) | 0.0018 (10) | 0.0084 (11) | −0.0019 (12) |
| C2 | 0.0350 (11) | 0.0592 (15) | 0.0600 (16) | −0.0068 (11) | 0.0068 (11) | −0.0103 (12) |
| C3 | 0.0296 (11) | 0.0649 (15) | 0.0623 (16) | −0.0018 (10) | 0.0015 (11) | −0.0110 (13) |
| C4 | 0.0348 (12) | 0.0562 (15) | 0.087 (2) | 0.0059 (11) | 0.0041 (13) | −0.0115 (14) |
| C5 | 0.0379 (12) | 0.0535 (14) | 0.085 (2) | −0.0026 (11) | 0.0075 (13) | −0.0096 (14) |
| C6 | 0.0303 (10) | 0.0581 (14) | 0.0578 (15) | −0.0025 (10) | 0.0068 (10) | −0.0109 (12) |
| C7 | 0.0326 (11) | 0.0568 (14) | 0.0549 (15) | −0.0021 (10) | 0.0063 (10) | −0.0113 (12) |
| C8 | 0.0308 (11) | 0.0706 (16) | 0.0440 (13) | −0.0032 (10) | 0.0034 (10) | −0.0065 (12) |
| C9 | 0.0314 (10) | 0.0508 (13) | 0.0445 (13) | 0.0033 (9) | 0.0050 (10) | −0.0043 (11) |
| C10 | 0.0605 (15) | 0.0619 (16) | 0.0481 (15) | 0.0093 (13) | −0.0046 (12) | 0.0023 (13) |

| | | | | | |
|---|---|---|---|---|---|
| C11 | 0.082 (2) | 0.0491 (15) | 0.071 (2) | 0.0130 (14) | 0.0040 (16) | 0.0051 (14) |
| C12 | 0.0579 (15) | 0.0527 (14) | 0.0610 (18) | 0.0018 (12) | 0.0101 (13) | −0.0101 (13) |
| C13 | 0.0507 (14) | 0.0624 (16) | 0.0452 (14) | −0.0022 (12) | 0.0007 (11) | −0.0021 (12) |
| C14 | 0.0412 (12) | 0.0486 (13) | 0.0470 (14) | 0.0024 (10) | 0.0020 (11) | 0.0019 (11) |
| C15 | 0.0457 (14) | 0.099 (2) | 0.077 (2) | −0.0327 (14) | 0.0223 (14) | −0.0379 (17) |
| C16 | 0.0325 (11) | 0.0570 (15) | 0.0620 (17) | −0.0094 (10) | 0.0105 (11) | −0.0123 (13) |
| C17 | 0.0631 (18) | 0.0624 (18) | 0.120 (3) | −0.0035 (15) | 0.0364 (19) | 0.007 (2) |
| C18 | 0.091 (3) | 0.065 (2) | 0.245 (7) | −0.025 (2) | 0.095 (4) | −0.060 (4) |
| C19 | 0.088 (3) | 0.165 (6) | 0.155 (5) | −0.062 (4) | 0.062 (4) | −0.102 (5) |
| C20 | 0.076 (2) | 0.184 (5) | 0.067 (2) | −0.029 (3) | 0.0154 (19) | −0.026 (3) |
| C21 | 0.0535 (16) | 0.088 (2) | 0.080 (2) | −0.0048 (15) | 0.0135 (15) | −0.0103 (19) |
| C22 | 0.0619 (17) | 0.0548 (16) | 0.112 (3) | −0.0076 (14) | 0.0124 (17) | −0.0017 (17) |
| C23 | 0.0445 (14) | 0.085 (2) | 0.095 (2) | −0.0043 (14) | 0.0199 (16) | −0.0046 (19) |
| C24 | 0.067 (2) | 0.056 (2) | 0.251 (6) | 0.0080 (16) | 0.009 (3) | 0.000 (3) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Br1—C12 | 1.885 (3) | C10—H10A | 0.9300 |
| S1—C8 | 1.664 (2) | C11—C12 | 1.379 (4) |
| F1—C17 | 1.349 (5) | C11—H11A | 0.9300 |
| F2—C21 | 1.344 (4) | C12—C13 | 1.370 (4) |
| O1—C2 | 1.359 (3) | C13—C14 | 1.383 (3) |
| O1—C22 | 1.418 (3) | C13—H13A | 0.9300 |
| O2—C3 | 1.376 (3) | C14—H14A | 0.9300 |
| O2—C23 | 1.411 (4) | C15—C16 | 1.491 (4) |
| O3—C4 | 1.362 (3) | C15—H15A | 0.9700 |
| O3—C24 | 1.403 (4) | C15—H15B | 0.9700 |
| N1—C8 | 1.384 (3) | C16—C17 | 1.363 (4) |
| N1—C7 | 1.386 (3) | C16—C21 | 1.378 (4) |
| N1—C9 | 1.429 (3) | C17—C18 | 1.363 (7) |
| N2—C7 | 1.294 (3) | C18—C19 | 1.372 (8) |
| N2—N3 | 1.381 (3) | C18—H18A | 0.9300 |
| N3—C8 | 1.342 (3) | C19—C20 | 1.319 (7) |
| N3—C15 | 1.461 (3) | C19—H19A | 0.9300 |
| C1—C6 | 1.384 (3) | C20—C21 | 1.367 (6) |
| C1—C2 | 1.395 (3) | C20—H20A | 0.9300 |
| C1—H1A | 0.9300 | C22—H22A | 0.9600 |
| C2—C3 | 1.386 (3) | C22—H22B | 0.9600 |
| C3—C4 | 1.381 (4) | C22—H22C | 0.9600 |
| C4—C5 | 1.395 (3) | C23—H23A | 0.9600 |
| C5—C6 | 1.387 (3) | C23—H23B | 0.9600 |
| C5—H5A | 0.9300 | C23—H23C | 0.9600 |
| C6—C7 | 1.475 (3) | C24—H24A | 0.9600 |
| C9—C14 | 1.376 (3) | C24—H24B | 0.9600 |
| C9—C10 | 1.383 (3) | C24—H24C | 0.9600 |
| C10—C11 | 1.375 (4) | | |
| C2—O1—C22 | 118.1 (2) | C12—C13—H13A | 120.2 |
| C3—O2—C23 | 114.8 (2) | C14—C13—H13A | 120.2 |
| C4—O3—C24 | 118.3 (2) | C9—C14—C13 | 119.4 (2) |

| | | | |
|---|---|---|---|
| C8—N1—C7 | 107.74 (19) | C9—C14—H14A | 120.3 |
| C8—N1—C9 | 122.63 (19) | C13—C14—H14A | 120.3 |
| C7—N1—C9 | 129.08 (17) | N3—C15—C16 | 114.0 (2) |
| C7—N2—N3 | 104.45 (19) | N3—C15—H15A | 108.8 |
| C8—N3—N2 | 113.36 (18) | C16—C15—H15A | 108.8 |
| C8—N3—C15 | 124.4 (2) | N3—C15—H15B | 108.8 |
| N2—N3—C15 | 121.2 (2) | C16—C15—H15B | 108.8 |
| C6—C1—C2 | 119.3 (2) | H15A—C15—H15B | 107.7 |
| C6—C1—H1A | 120.3 | C17—C16—C21 | 113.4 (3) |
| C2—C1—H1A | 120.3 | C17—C16—C15 | 123.5 (3) |
| O1—C2—C3 | 115.9 (2) | C21—C16—C15 | 122.8 (3) |
| O1—C2—C1 | 123.9 (2) | F1—C17—C18 | 119.2 (4) |
| C3—C2—C1 | 120.2 (2) | F1—C17—C16 | 115.8 (4) |
| O2—C3—C4 | 119.8 (2) | C18—C17—C16 | 124.9 (4) |
| O2—C3—C2 | 119.9 (2) | C17—C18—C19 | 116.8 (4) |
| C4—C3—C2 | 120.1 (2) | C17—C18—H18A | 121.6 |
| O3—C4—C3 | 115.4 (2) | C19—C18—H18A | 121.6 |
| O3—C4—C5 | 124.5 (2) | C20—C19—C18 | 122.5 (5) |
| C3—C4—C5 | 120.1 (2) | C20—C19—H19A | 118.7 |
| C6—C5—C4 | 119.5 (2) | C18—C19—H19A | 118.7 |
| C6—C5—H5A | 120.3 | C19—C20—C21 | 117.8 (5) |
| C4—C5—H5A | 120.3 | C19—C20—H20A | 121.1 |
| C1—C6—C5 | 120.7 (2) | C21—C20—H20A | 121.1 |
| C1—C6—C7 | 121.8 (2) | F2—C21—C20 | 119.1 (4) |
| C5—C6—C7 | 117.5 (2) | F2—C21—C16 | 116.4 (3) |
| N2—C7—N1 | 111.06 (19) | C20—C21—C16 | 124.5 (4) |
| N2—C7—C6 | 123.4 (2) | O1—C22—H22A | 109.5 |
| N1—C7—C6 | 125.6 (2) | O1—C22—H22B | 109.5 |
| N3—C8—N1 | 103.31 (19) | H22A—C22—H22B | 109.5 |
| N3—C8—S1 | 128.53 (17) | O1—C22—H22C | 109.5 |
| N1—C8—S1 | 128.1 (2) | H22A—C22—H22C | 109.5 |
| C14—C9—C10 | 120.7 (2) | H22B—C22—H22C | 109.5 |
| C14—C9—N1 | 119.6 (2) | O2—C23—H23A | 109.5 |
| C10—C9—N1 | 119.7 (2) | O2—C23—H23B | 109.5 |
| C11—C10—C9 | 119.8 (2) | H23A—C23—H23B | 109.5 |
| C11—C10—H10A | 120.1 | O2—C23—H23C | 109.5 |
| C9—C10—H10A | 120.1 | H23A—C23—H23C | 109.5 |
| C10—C11—C12 | 119.2 (2) | H23B—C23—H23C | 109.5 |
| C10—C11—H11A | 120.4 | O3—C24—H24A | 109.5 |
| C12—C11—H11A | 120.4 | O3—C24—H24B | 109.5 |
| C13—C12—C11 | 121.2 (2) | H24A—C24—H24B | 109.5 |
| C13—C12—Br1 | 119.0 (2) | O3—C24—H24C | 109.5 |
| C11—C12—Br1 | 119.8 (2) | H24A—C24—H24C | 109.5 |
| C12—C13—C14 | 119.6 (2) | H24B—C24—H24C | 109.5 |
| | | | |
| C7—N2—N3—C8 | 1.8 (3) | C15—N3—C8—S1 | 5.6 (4) |
| C7—N2—N3—C15 | 170.8 (3) | C7—N1—C8—N3 | 2.5 (3) |
| C22—O1—C2—C3 | 168.4 (3) | C9—N1—C8—N3 | 174.7 (2) |
| C22—O1—C2—C1 | −10.7 (4) | C7—N1—C8—S1 | −174.3 (2) |
| C6—C1—C2—O1 | 178.1 (3) | C9—N1—C8—S1 | −2.1 (4) |

| | | | |
|---|---|---|---|
| C6—C1—C2—C3 | −0.9 (4) | C8—N1—C9—C14 | −110.9 (3) |
| C23—O2—C3—C4 | −89.1 (3) | C7—N1—C9—C14 | 59.5 (3) |
| C23—O2—C3—C2 | 95.5 (3) | C8—N1—C9—C10 | 67.5 (3) |
| O1—C2—C3—O2 | −3.8 (4) | C7—N1—C9—C10 | −122.1 (3) |
| C1—C2—C3—O2 | 175.3 (2) | C14—C9—C10—C11 | 0.5 (4) |
| O1—C2—C3—C4 | −179.2 (3) | N1—C9—C10—C11 | −178.0 (2) |
| C1—C2—C3—C4 | 0.0 (4) | C9—C10—C11—C12 | −0.4 (4) |
| C24—O3—C4—C3 | 177.9 (4) | C10—C11—C12—C13 | −0.6 (5) |
| C24—O3—C4—C5 | −2.6 (6) | C10—C11—C12—Br1 | 178.9 (2) |
| O2—C3—C4—O3 | 5.4 (4) | C11—C12—C13—C14 | 1.5 (4) |
| C2—C3—C4—O3 | −179.2 (3) | Br1—C12—C13—C14 | −177.93 (19) |
| O2—C3—C4—C5 | −174.1 (3) | C10—C9—C14—C13 | 0.5 (4) |
| C2—C3—C4—C5 | 1.3 (5) | N1—C9—C14—C13 | 178.9 (2) |
| O3—C4—C5—C6 | 179.0 (3) | C12—C13—C14—C9 | −1.5 (4) |
| C3—C4—C5—C6 | −1.6 (5) | C8—N3—C15—C16 | −146.7 (3) |
| C2—C1—C6—C5 | 0.7 (4) | N2—N3—C15—C16 | 45.6 (4) |
| C2—C1—C6—C7 | −177.9 (2) | N3—C15—C16—C17 | −106.4 (3) |
| C4—C5—C6—C1 | 0.6 (5) | N3—C15—C16—C21 | 78.7 (3) |
| C4—C5—C6—C7 | 179.2 (3) | C21—C16—C17—F1 | 177.9 (3) |
| N3—N2—C7—N1 | −0.1 (3) | C15—C16—C17—F1 | 2.5 (4) |
| N3—N2—C7—C6 | −178.9 (2) | C21—C16—C17—C18 | −0.4 (4) |
| C8—N1—C7—N2 | −1.6 (3) | C15—C16—C17—C18 | −175.8 (3) |
| C9—N1—C7—N2 | −173.1 (2) | F1—C17—C18—C19 | −177.7 (4) |
| C8—N1—C7—C6 | 177.2 (3) | C16—C17—C18—C19 | 0.5 (6) |
| C9—N1—C7—C6 | 5.7 (4) | C17—C18—C19—C20 | −0.1 (7) |
| C1—C6—C7—N2 | −153.5 (3) | C18—C19—C20—C21 | −0.3 (7) |
| C5—C6—C7—N2 | 27.9 (4) | C19—C20—C21—F2 | −178.6 (3) |
| C1—C6—C7—N1 | 27.9 (4) | C19—C20—C21—C16 | 0.4 (6) |
| C5—C6—C7—N1 | −150.7 (3) | C17—C16—C21—F2 | 178.9 (3) |
| N2—N3—C8—N1 | −2.7 (3) | C15—C16—C21—F2 | −5.7 (4) |
| C15—N3—C8—N1 | −171.3 (3) | C17—C16—C21—C20 | −0.1 (4) |
| N2—N3—C8—S1 | 174.1 (2) | C15—C16—C21—C20 | 175.3 (3) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C13—H13A···O1[i] | 0.93 | 2.54 | 3.284 (3) | 137 |
| C14—H14A···O2[i] | 0.93 | 2.40 | 3.142 (3) | 137 |

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

**Fig. 1**

**Fig. 2**