

Crystal structure of (Z)-3-{3-(4-chlorophenyl)-2-[(4-chlorophenyl)imino]-2,3-dihydrothiazol-4-yl}-2H-chromen-2-one

M. Kayalvizhi,^a G. Vasuki,^{a*} R. Raj Kumar^b and V. Rajeswar Rao^b

^aDepartment of Physics, Kunthavai Naachiar Government Arts College (W) (Autonomous), Thanjavur 613 007, Tamilnadu, India, and ^bDepartment of Chemistry, National Institute of Technology, Warangal 506 004, Telangana, India.
*Correspondence e-mail: vasuki.arasi@yahoo.com

Received 26 October 2014; accepted 11 November 2014

Edited by G. Smith, Queensland University of Technology, Australia

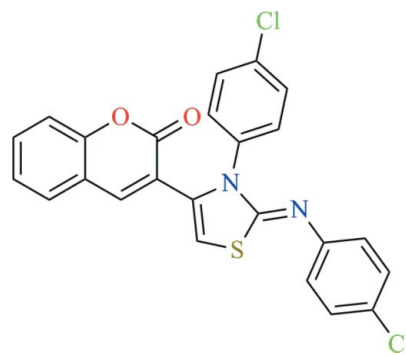
In the title compound, C₂₄H₁₄Cl₂N₂O₂S, the 2H-chromene ring system is approximately planar, with a maximum deviation of 0.025 (2) Å. The thiazole ring is almost planar, with an r.m.s. deviation of 0.0022 Å, and makes a dihedral angle of 58.52 (7)° with the chromene ring system. The chromene ring system is inclined at angles of 58.3 (1) and 55.39 (9)° with respect to the two chlorophenyl rings. The two chlorophenyl rings show significant deviation from coplanarity, with a dihedral angle between them of 47.69 (8)°. The crystal structure features C—H...Cl interactions extending in (100) and propagating along the *a*-axis direction and weak π – π interactions [centroid–centroid separation = 3.867 (2) Å].

Keywords: crystal structure; 2H-chromen-2-one; bioactivity; hydrogen bonding; π – π interactions.

CCDC reference: 1027667

1. Related literature

For the bioactivity of coumarin, see: Yusufzai *et al.* (2012). For related structures, see: Arshad, Osman, Chan *et al.* (2010); Arshad, Osman, Lam *et al.* (2010*a,b*). For synthetic chemistry, medicinal chemistry, photochemistry and solid-state chemistry applications of coumarin derivatives, see: Chopra *et al.* (2009). For the synthesis, see: Raj Kumar & Rajeswar Rao (2014).



2. Experimental

2.1. Crystal data

C₂₄H₁₄Cl₂N₂O₂S
M_r = 465.33
Monoclinic, *P*2₁
a = 9.1491 (7) Å
b = 10.3099 (8) Å
c = 11.9347 (10) Å
 β = 111.587 (2)°

V = 1046.80 (14) Å³
Z = 2
Mo *K*α radiation
 μ = 0.44 mm⁻¹
T = 296 K
0.35 × 0.30 × 0.25 mm

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1999)
*T*_{min} = 0.897, *T*_{max} = 1.000

15409 measured reflections
5549 independent reflections
4070 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.024

2.3. Refinement

R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.075
S = 1.03
5549 reflections
280 parameters
1 restraint
H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.17 e Å⁻³

$\Delta\rho_{\min}$ = -0.20 e Å⁻³
Absolute structure: Flack *x* determined using 1604 quotients [(*I*⁺) - (*I*⁻)] / [(*I*⁺) + (*I*⁻)] (Parsons *et al.*, 2013)
Absolute structure parameter: -0.004 (19)

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 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2009).

Acknowledgements

The authors thank the Sophisticated Analytical Instrument Facility, IITM, Chennai 600 036, Tamilnadu, India, for the data collection.

Supporting information for this paper is available from the IUCr electronic archives (Reference: ZS2320).

References

- Arshad, A., Osman, H., Chan, K. L., Yeap, C. S. & Fun, H.-K. (2010). *Acta Cryst.* **E66**, o1788–o1789.
- Arshad, A., Osman, H., Lam, C. K., Quah, C. K. & Fun, H.-K. (2010a). *Acta Cryst.* **E66**, o1632–o1633.
- Arshad, A., Osman, H., Lam, C. K., Quah, C. K. & Fun, H.-K. (2010b). *Acta Cryst.* **E66**, o1446–o1447.
- Bruker (1999). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2004). *APEX2*, *SAINT-Plus* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chopra, D., Choudhury, A. R., Venugopala, K. N., Govender, T., Kruger, H. G., Maguire, G. E. M. & Guru Row, T. N. (2009). *Acta Cryst.* **E65**, o3047–o3048.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Raj Kumar, R. & Rajeswar Rao, V. (2014). *Synth. Commun.* **44**, 1301–1306.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Yusufzai, S. K., Osman, H., Rahim, A. S. A., Arshad, S. & Razak, I. A. (2012). *Acta Cryst.* **E68**, o2416–o2417.

supporting information

Acta Cryst. (2014). E70, o1268–o1269 [doi:10.1107/S1600536814024775]

Crystal structure of (Z)-3-{3-(4-chlorophenyl)-2-[(4-chlorophenyl)imino]-2,3-dihydrothiazol-4-yl}-2H-chromen-2-one

M. Kayalvizhi, G. Vasuki, R. Raj Kumar and V. Rajeswar Rao

S1. Comment

Compounds containing the coumarin moiety exhibit useful and diverse biological activities (Yusufzai *et al.*, 2012). Coumarins are an important class of organic compounds and have been extensively studied. Such molecules of vast structural diversity find useful applications in several areas of synthetic chemistry, medicinal chemistry and photochemistry. The formation of [2 + 2] cycloaddition products upon irradiation of coumarin and its derivatives has contributed immensely to the area of solid-state chemistry. Several substituted coumarin derivatives find applications in the dye industry and in the area of laser dyes based on the fact that such compounds show state dependent variations in their static dipole moments. The geometry and molecular packing patterns of several coumarins derivatives have been studied to evaluate the features of non-covalent interactions (Chopra *et al.*, 2009). Some of the coumarin derivatives have been found to be useful in photochemotherapy, antitumour, anti-HIV therapy, anti-bacterial, anticoagulant, anti-fungal, cytotoxic activities, free radical scavengers and enzyme inhibiting agents. The related compounds whose structures have been solved by X-ray are 3-{2-[2-(diphenylmethylene)hydrazinyl]thiazol-4-yl}-2H-chromen-2-one (Arshad, Osman, Chan *et al.*, 2010), (Z)-3-(2-{2-[1-(4-hydroxyphenyl)ethylidene]hydrazin-1-yl}-1,3-thiazol-4-yl)-2H-chromen-2-one (Arshad, Osman, Lam *et al.*, 2010a) and 3-{2-[2-(2-fluorobenzylidene)hydrazinyl]-1,3-thiazol-4-yl}-2H-chromen-2-one (Arshad, Osman, Lam *et al.*, 2010b). The title compound, C₂₄H₁₄Cl₂N₂O₂S, (Fig. 1), is a new derivative of dihydrothiazoyl coumarin. We present herein its crystal structure.

The 2H-chromene (O1/C1–C9/O2) ring system is approximately planar, with the maximum deviation of -0.025 (2) Å at atom O1. The thiazole ring (S1/N1/C10–C12) is almost planar with a r.m.s. deviation of 0.0022 Å and makes a dihedral angle of 58.52 (7)° with the chromene ring. The chromene ring system is inclined at angles of 58.3 (1)° and 55.39 (9)° with respect to the two chlorophenyl rings (C13–C18/C11) and (C19–C24/C12), respectively. The two chlorophenyl rings show significant deviation from coplanarity, with a dihedral angle between the two planes of 47.69 (8)°. The sum of bond angles around N1 [359.79 (5)°] indicates that atom N exhibits *sp*² hybridization. Torsion angles C1–C2–C10–N1 = -58.5 (4)° and C10–N1–C22–C23 = -51.8 (4)° indicate that the chromene ring and the chlorophenyl ring are substituted *synclinally* to the thiazole ring at atoms C2 and C22, respectively. The torsion angle C22–N1–C12–N2 [6.4 (4)°] indicates that the two chlorophenyl rings have a *Z*-configuration across the N1–C12 bond. In the crystal, a short intermolecular C3–Hⁱ⋯Clⁱ contact is observed [3.282 (3) Å] [symmetry code: (i) *x*, *y* - 1, *z*] together with second longer C23–Hⁱⁱ⋯Clⁱⁱ contact is observed between C23 and Clⁱⁱ [3.547 (3) Å] [symmetry code: *x* + 1, *y*, *z* + 1] (Fig. 2). Inter-ring π – π stacking interactions between the symmetry related C4–C9 ring (centroid Cg3) and the C13–C18ⁱⁱⁱ ring (centroid Cg4), with Cg3⋯Cg4 = 3.867 (2) Å (symmetry code: (iii) *x* + 1, *y*, *z* + 1) further stabilize the crystal structure (Fig. 3).

S2. Experimental

The compound was synthesized according to the published procedure (Raj Kumar & Rajeswar Rao, 2014).

S3. Refinement

All the H atoms were positioned geometrically and treated as riding on their parent atoms: C—H = 0.93 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Although of no relevance in this achiral structure, the Flack factor obtained (Parsons *et al.*, 2013) was -0.004 (19).

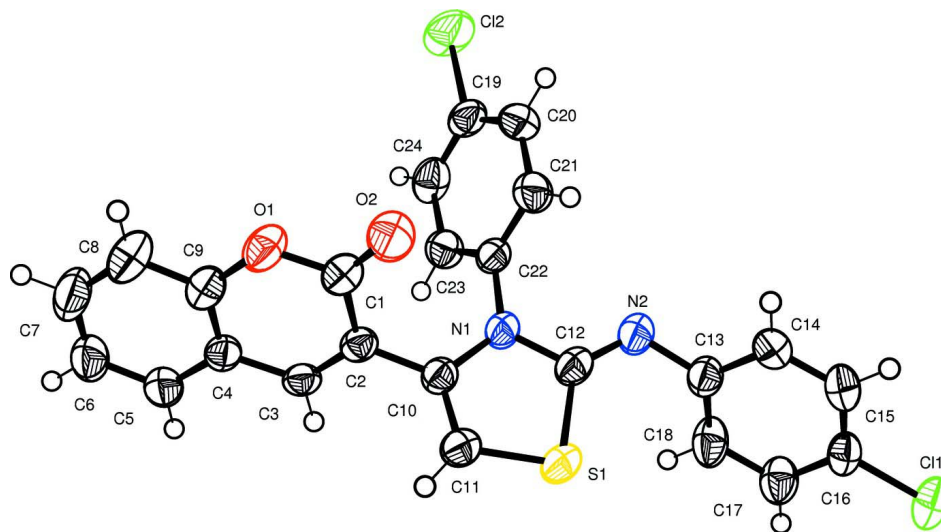


Figure 1

The molecular structure of the title compound showing atom numbering, with displacement ellipsoids drawn at the 50% probability level.

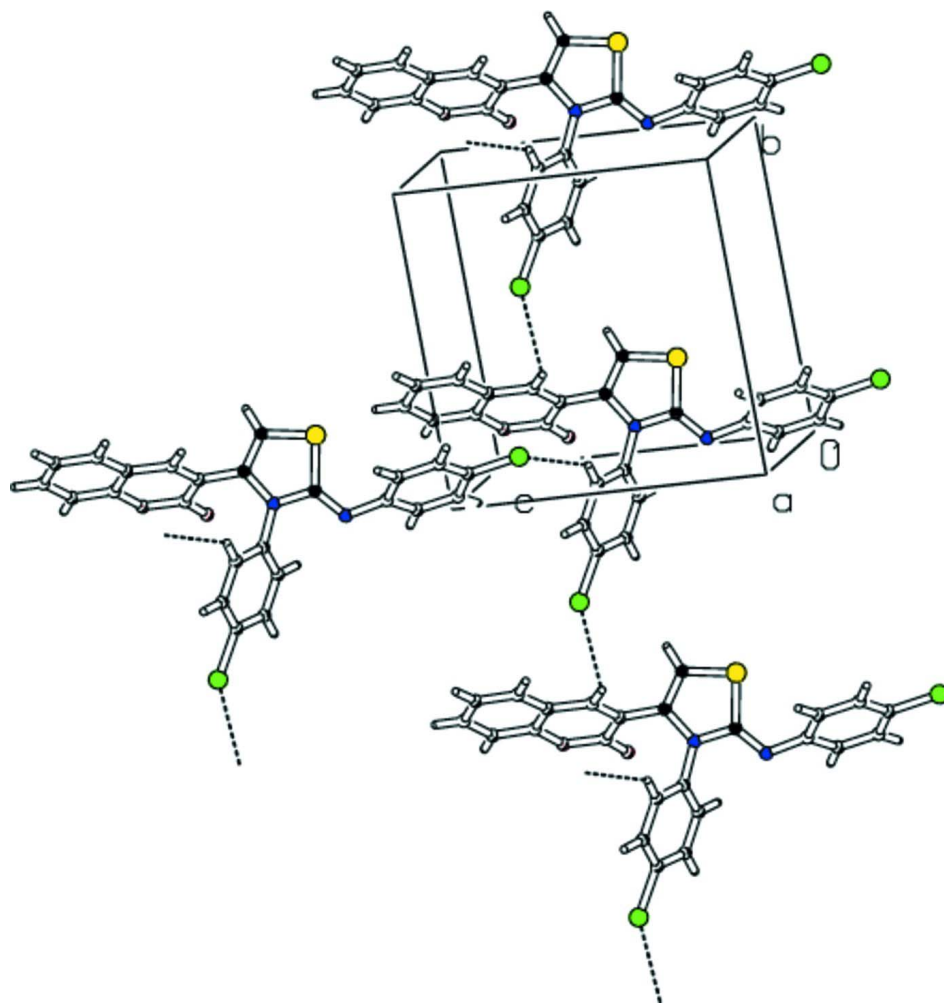
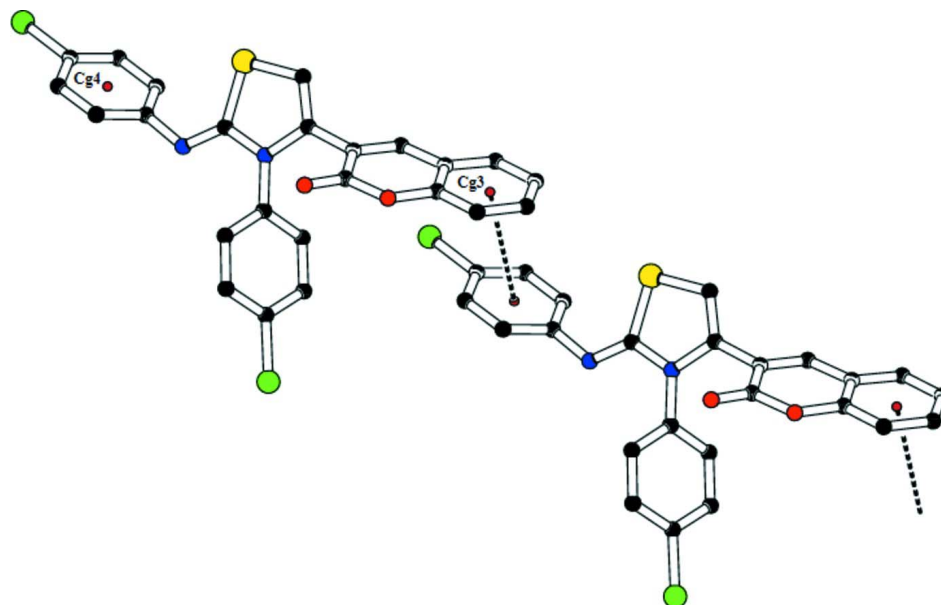


Figure 2

Crystal packing of the title compound in the unit cell, viewed along the *a* axis, showing C—H...Cl interactions as dashed lines.

**Figure 3**

The partial packing of the title compound, showing the π - π interactions.

(Z)-3-{3-(4-Chlorophenyl)-2-[(4-chlorophenyl)imino]-2,3-dihydrothiazol-4-yl}-2H-chromen-2-one

Crystal data

$C_{24}H_{14}Cl_2N_2O_2S$

$M_r = 465.33$

Monoclinic, $P2_1$

$a = 9.1491$ (7) Å

$b = 10.3099$ (8) Å

$c = 11.9347$ (10) Å

$\beta = 111.587$ (2)°

$V = 1046.80$ (14) Å³

$Z = 2$

$F(000) = 476$

$D_x = 1.476$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5853 reflections

$\theta = 4.8$ – 29.9 °

$\mu = 0.44$ mm⁻¹

$T = 296$ K

Block, colourless

$0.35 \times 0.30 \times 0.25$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1999)

$T_{\min} = 0.897$, $T_{\max} = 1.000$

15409 measured reflections

5549 independent reflections

4070 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 30.2$ °, $\theta_{\min} = 2.4$ °

$h = -12 \rightarrow 12$

$k = -13 \rightarrow 14$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.075$

$S = 1.03$

5549 reflections

280 parameters

1 restraint

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 0.1767P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using
1604 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: -0.004 (19)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.73427 (9)	0.67172 (10)	1.28483 (6)	0.0611 (2)
Cl2	0.07802 (15)	0.15926 (9)	0.32829 (9)	0.0911 (3)
S1	0.42551 (10)	0.84490 (8)	0.71595 (7)	0.0526 (2)
O1	0.2030 (2)	0.7096 (2)	0.17243 (18)	0.0552 (6)
O2	0.3924 (2)	0.6405 (2)	0.33588 (19)	0.0611 (6)
N1	0.3118 (2)	0.6598 (2)	0.56482 (18)	0.0408 (5)
N2	0.4358 (3)	0.5837 (2)	0.7613 (2)	0.0536 (7)
C1	0.2735 (3)	0.7030 (3)	0.2954 (2)	0.0438 (7)
C2	0.1989 (3)	0.7740 (3)	0.3656 (2)	0.0366 (6)
C3	0.0669 (3)	0.8415 (3)	0.3101 (2)	0.0386 (6)
H3	0.0194	0.8846	0.3562	0.046*
C4	-0.0030 (3)	0.8489 (3)	0.1811 (2)	0.0392 (6)
C5	-0.1396 (4)	0.9181 (3)	0.1185 (3)	0.0511 (8)
H5	-0.1912	0.9631	0.1607	0.061*
C6	-0.1983 (4)	0.9202 (4)	-0.0050 (3)	0.0606 (9)
H6	-0.2893	0.9667	-0.0465	0.073*
C7	-0.1228 (4)	0.8536 (4)	-0.0675 (3)	0.0690 (10)
H7	-0.1631	0.8562	-0.1513	0.083*
C8	0.0110 (4)	0.7834 (4)	-0.0087 (3)	0.0645 (9)
H8	0.0611	0.7378	-0.0515	0.077*
C9	0.0692 (3)	0.7822 (3)	0.1157 (2)	0.0452 (7)
C10	0.2782 (3)	0.7744 (3)	0.4978 (2)	0.0379 (6)
C11	0.3305 (4)	0.8795 (3)	0.5646 (3)	0.0462 (7)
H11	0.3174	0.9632	0.5333	0.055*
C12	0.3931 (3)	0.6762 (3)	0.6869 (2)	0.0428 (6)
C13	0.5081 (3)	0.6096 (3)	0.8852 (3)	0.0453 (7)
C14	0.6503 (4)	0.5525 (3)	0.9501 (3)	0.0551 (8)
H14	0.6992	0.5005	0.9106	0.066*
C15	0.7211 (4)	0.5712 (3)	1.0723 (3)	0.0559 (9)
H15	0.8178	0.5330	1.1149	0.067*
C16	0.6480 (3)	0.6468 (3)	1.1310 (2)	0.0422 (6)
C17	0.5071 (3)	0.7039 (3)	1.0692 (3)	0.0531 (8)
H17	0.4584	0.7554	1.1092	0.064*
C18	0.4369 (3)	0.6845 (4)	0.9460 (3)	0.0556 (8)
H18	0.3402	0.7227	0.9036	0.067*

C19	0.1469 (4)	0.3047 (3)	0.4032 (3)	0.0506 (8)
C20	0.3036 (4)	0.3174 (3)	0.4712 (3)	0.0536 (8)
H20	0.3723	0.2485	0.4792	0.064*
C21	0.3576 (4)	0.4336 (3)	0.5275 (3)	0.0492 (8)
H21	0.4636	0.4437	0.5745	0.059*
C22	0.2553 (3)	0.5348 (3)	0.5145 (2)	0.0377 (6)
C23	0.0977 (3)	0.5194 (3)	0.4499 (3)	0.0443 (7)
H23	0.0285	0.5871	0.4448	0.053*
C24	0.0419 (4)	0.4032 (3)	0.3925 (3)	0.0527 (8)
H24	-0.0645	0.3920	0.3476	0.063*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0589 (4)	0.0805 (6)	0.0361 (4)	-0.0094 (4)	0.0086 (3)	0.0030 (4)
C12	0.1509 (9)	0.0438 (4)	0.0690 (6)	-0.0333 (6)	0.0292 (6)	-0.0135 (5)
S1	0.0634 (5)	0.0460 (4)	0.0382 (4)	-0.0074 (4)	0.0069 (3)	-0.0095 (3)
O1	0.0514 (11)	0.0756 (15)	0.0401 (11)	0.0026 (11)	0.0187 (10)	-0.0100 (10)
O2	0.0481 (12)	0.0787 (17)	0.0577 (13)	0.0119 (12)	0.0209 (10)	-0.0019 (12)
N1	0.0441 (12)	0.0374 (11)	0.0330 (11)	-0.0043 (11)	0.0050 (9)	-0.0020 (11)
N2	0.0641 (17)	0.0458 (15)	0.0380 (13)	-0.0036 (12)	0.0037 (12)	-0.0006 (11)
C1	0.0427 (15)	0.0492 (16)	0.0404 (15)	-0.0036 (14)	0.0162 (13)	-0.0047 (13)
C2	0.0404 (15)	0.0341 (13)	0.0357 (14)	-0.0053 (12)	0.0144 (12)	-0.0038 (11)
C3	0.0476 (15)	0.0300 (12)	0.0390 (14)	-0.0045 (13)	0.0170 (12)	-0.0054 (12)
C4	0.0445 (14)	0.0337 (13)	0.0367 (13)	-0.0076 (13)	0.0117 (12)	-0.0020 (12)
C5	0.0561 (19)	0.0434 (16)	0.0460 (17)	0.0003 (14)	0.0096 (15)	0.0001 (14)
C6	0.063 (2)	0.058 (2)	0.0460 (18)	0.0005 (17)	0.0026 (16)	0.0053 (16)
C7	0.078 (2)	0.082 (2)	0.0355 (16)	-0.005 (2)	0.0079 (17)	0.0021 (19)
C8	0.066 (2)	0.088 (3)	0.0402 (17)	-0.007 (2)	0.0208 (16)	-0.0091 (18)
C9	0.0461 (16)	0.0518 (17)	0.0372 (15)	-0.0077 (14)	0.0146 (13)	-0.0026 (13)
C10	0.0371 (14)	0.0396 (15)	0.0352 (14)	-0.0007 (12)	0.0112 (12)	-0.0027 (12)
C11	0.0566 (19)	0.0402 (17)	0.0398 (16)	-0.0039 (13)	0.0154 (14)	-0.0043 (12)
C12	0.0399 (13)	0.0471 (17)	0.0370 (14)	-0.0047 (14)	0.0090 (11)	-0.0071 (14)
C13	0.0475 (16)	0.0430 (15)	0.0381 (15)	-0.0052 (13)	0.0069 (13)	0.0019 (13)
C14	0.066 (2)	0.0477 (17)	0.0456 (17)	0.0145 (16)	0.0142 (16)	0.0030 (14)
C15	0.0490 (18)	0.061 (2)	0.0464 (18)	0.0120 (15)	0.0039 (15)	0.0077 (15)
C16	0.0402 (14)	0.0489 (16)	0.0332 (13)	-0.0061 (13)	0.0086 (11)	0.0064 (13)
C17	0.0462 (16)	0.072 (2)	0.0430 (16)	0.0079 (16)	0.0182 (13)	0.0052 (15)
C18	0.0384 (14)	0.081 (2)	0.0429 (16)	0.0096 (17)	0.0095 (13)	0.0070 (18)
C19	0.079 (2)	0.0358 (15)	0.0362 (15)	-0.0115 (15)	0.0207 (15)	-0.0025 (12)
C20	0.072 (2)	0.0378 (17)	0.0506 (18)	0.0081 (14)	0.0218 (17)	0.0017 (13)
C21	0.0434 (17)	0.0474 (18)	0.0496 (18)	0.0029 (14)	0.0089 (14)	-0.0011 (14)
C22	0.0441 (16)	0.0356 (14)	0.0315 (13)	-0.0028 (12)	0.0118 (12)	-0.0021 (11)
C23	0.0390 (15)	0.0445 (17)	0.0459 (16)	-0.0006 (12)	0.0114 (13)	-0.0011 (13)
C24	0.0486 (17)	0.0565 (19)	0.0447 (17)	-0.0186 (16)	0.0075 (14)	0.0003 (15)

Geometric parameters (Å, °)

C11—C16	1.731 (3)	C8—C9	1.380 (4)
C12—C19	1.741 (3)	C8—H8	0.9300
S1—C11	1.729 (3)	C10—C11	1.326 (4)
S1—C12	1.777 (3)	C11—H11	0.9300
O1—C1	1.371 (3)	C13—C18	1.376 (4)
O1—C9	1.382 (4)	C13—C14	1.378 (4)
O2—C1	1.203 (3)	C14—C15	1.374 (4)
N1—C12	1.381 (3)	C14—H14	0.9300
N1—C10	1.396 (4)	C15—C16	1.375 (4)
N1—C22	1.436 (3)	C15—H15	0.9300
N2—C12	1.263 (4)	C16—C17	1.362 (4)
N2—C13	1.406 (4)	C17—C18	1.386 (4)
C1—C2	1.457 (4)	C17—H17	0.9300
C2—C3	1.339 (4)	C18—H18	0.9300
C2—C10	1.474 (4)	C19—C20	1.369 (5)
C3—C4	1.435 (3)	C19—C24	1.371 (5)
C3—H3	0.9300	C20—C21	1.373 (4)
C4—C9	1.378 (4)	C20—H20	0.9300
C4—C5	1.394 (4)	C21—C22	1.371 (4)
C5—C6	1.371 (4)	C21—H21	0.9300
C5—H5	0.9300	C22—C23	1.371 (4)
C6—C7	1.372 (5)	C23—C24	1.381 (4)
C6—H6	0.9300	C23—H23	0.9300
C7—C8	1.372 (5)	C24—H24	0.9300
C7—H7	0.9300		
C11—S1—C12	90.84 (13)	N2—C12—N1	123.8 (3)
C1—O1—C9	122.3 (2)	N2—C12—S1	128.0 (2)
C12—N1—C10	114.9 (2)	N1—C12—S1	108.2 (2)
C12—N1—C22	121.5 (2)	C18—C13—C14	118.4 (3)
C10—N1—C22	123.41 (19)	C18—C13—N2	122.1 (3)
C12—N2—C13	120.0 (3)	C14—C13—N2	119.4 (3)
O2—C1—O1	117.1 (3)	C15—C14—C13	121.0 (3)
O2—C1—C2	125.8 (3)	C15—C14—H14	119.5
O1—C1—C2	117.1 (2)	C13—C14—H14	119.5
C3—C2—C1	120.3 (2)	C14—C15—C16	119.5 (3)
C3—C2—C10	121.8 (2)	C14—C15—H15	120.2
C1—C2—C10	117.8 (2)	C16—C15—H15	120.2
C2—C3—C4	121.5 (3)	C17—C16—C15	120.7 (3)
C2—C3—H3	119.2	C17—C16—C11	118.8 (2)
C4—C3—H3	119.2	C15—C16—C11	120.5 (2)
C9—C4—C5	118.3 (3)	C16—C17—C18	119.2 (3)
C9—C4—C3	117.6 (2)	C16—C17—H17	120.4
C5—C4—C3	124.1 (3)	C18—C17—H17	120.4
C6—C5—C4	120.2 (3)	C13—C18—C17	121.1 (3)
C6—C5—H5	119.9	C13—C18—H18	119.5

C4—C5—H5	119.9	C17—C18—H18	119.5
C5—C6—C7	120.0 (3)	C20—C19—C24	121.9 (3)
C5—C6—H6	120.0	C20—C19—C12	119.3 (3)
C7—C6—H6	120.0	C24—C19—C12	118.7 (3)
C6—C7—C8	121.2 (3)	C19—C20—C21	118.9 (3)
C6—C7—H7	119.4	C19—C20—H20	120.5
C8—C7—H7	119.4	C21—C20—H20	120.5
C7—C8—C9	118.3 (3)	C22—C21—C20	120.0 (3)
C7—C8—H8	120.9	C22—C21—H21	120.0
C9—C8—H8	120.9	C20—C21—H21	120.0
C4—C9—C8	122.0 (3)	C23—C22—C21	120.6 (3)
C4—C9—O1	121.1 (2)	C23—C22—N1	118.7 (2)
C8—C9—O1	117.0 (3)	C21—C22—N1	120.7 (2)
C11—C10—N1	113.1 (2)	C22—C23—C24	120.0 (3)
C11—C10—C2	124.9 (3)	C22—C23—H23	120.0
N1—C10—C2	121.9 (2)	C24—C23—H23	120.0
C10—C11—S1	113.0 (2)	C19—C24—C23	118.5 (3)
C10—C11—H11	123.5	C19—C24—H24	120.7
S1—C11—H11	123.5	C23—C24—H24	120.7
C9—O1—C1—O2	-177.6 (3)	C13—N2—C12—N1	-175.3 (3)
C9—O1—C1—C2	1.5 (4)	C13—N2—C12—S1	5.4 (4)
O2—C1—C2—C3	179.3 (3)	C10—N1—C12—N2	-178.8 (3)
O1—C1—C2—C3	0.3 (4)	C22—N1—C12—N2	6.4 (4)
O2—C1—C2—C10	2.7 (4)	C10—N1—C12—S1	0.5 (3)
O1—C1—C2—C10	-176.4 (2)	C22—N1—C12—S1	-174.3 (2)
C1—C2—C3—C4	-1.5 (4)	C11—S1—C12—N2	178.9 (3)
C10—C2—C3—C4	175.0 (2)	C11—S1—C12—N1	-0.4 (2)
C2—C3—C4—C9	1.0 (4)	C12—N2—C13—C18	56.7 (4)
C2—C3—C4—C5	-179.7 (3)	C12—N2—C13—C14	-127.2 (3)
C9—C4—C5—C6	-0.7 (4)	C18—C13—C14—C15	-1.0 (5)
C3—C4—C5—C6	179.9 (3)	N2—C13—C14—C15	-177.2 (3)
C4—C5—C6—C7	0.2 (5)	C13—C14—C15—C16	0.8 (5)
C5—C6—C7—C8	0.5 (6)	C14—C15—C16—C17	-0.5 (5)
C6—C7—C8—C9	-0.6 (6)	C14—C15—C16—C11	179.9 (3)
C5—C4—C9—C8	0.6 (4)	C15—C16—C17—C18	0.4 (5)
C3—C4—C9—C8	-180.0 (3)	C11—C16—C17—C18	-180.0 (3)
C5—C4—C9—O1	-178.6 (3)	C14—C13—C18—C17	0.9 (5)
C3—C4—C9—O1	0.8 (4)	N2—C13—C18—C17	177.0 (3)
C7—C8—C9—C4	0.1 (5)	C16—C17—C18—C13	-0.6 (5)
C7—C8—C9—O1	179.3 (3)	C24—C19—C20—C21	-1.9 (5)
C1—O1—C9—C4	-2.0 (4)	C12—C19—C20—C21	178.3 (2)
C1—O1—C9—C8	178.7 (3)	C19—C20—C21—C22	-0.4 (5)
C12—N1—C10—C11	-0.4 (3)	C20—C21—C22—C23	3.0 (5)
C22—N1—C10—C11	174.3 (3)	C20—C21—C22—N1	-175.1 (3)
C12—N1—C10—C2	177.1 (2)	C12—N1—C22—C23	122.6 (3)
C22—N1—C10—C2	-8.2 (4)	C10—N1—C22—C23	-51.8 (4)
C3—C2—C10—C11	-58.0 (4)	C12—N1—C22—C21	-59.4 (4)

supporting information

C1—C2—C10—C11	118.6 (3)	C10—N1—C22—C21	126.3 (3)
C3—C2—C10—N1	124.9 (3)	C21—C22—C23—C24	-3.2 (4)
C1—C2—C10—N1	-58.5 (4)	N1—C22—C23—C24	174.9 (3)
N1—C10—C11—S1	0.0 (3)	C20—C19—C24—C23	1.7 (5)
C2—C10—C11—S1	-177.3 (2)	C12—C19—C24—C23	-178.6 (2)
C12—S1—C11—C10	0.2 (3)	C22—C23—C24—C19	0.9 (4)
