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5-(4-Methoxyphenyl)-1-[4-(4-methoxyphenyl)thiazol-2-yl]-3-[4-(prop-2-ynyloxy)phenyl]-4,5-dihydro-1*H*-pyrazole[1]

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[1] Dedicated to the memory of Professor Jerry P. Jasinski.

Keywords: crystal structure; pyrazoles; thiazoles; dihydropyrazoles.

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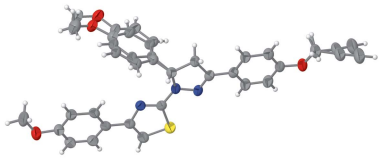
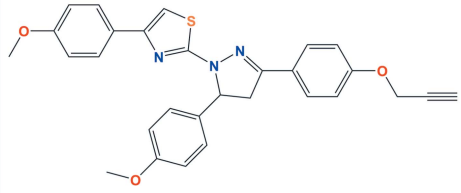
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{29}H_{25}N_3O_3S$, crystallizes in the monoclinic space group $P2_1/n$. The molecule contains a central four-ring system in which all of the rings are almost coplanar. Both the 4-methoxyphenyl ring and the prop-2-ynyloxy substituent are disordered over two equivalent conformations with occupancy ratios of 0.903 (2):0.097 (2) and 0.776 (5):0.224 (5), respectively. In the crystal, π–π interactions [centroid–centroid distance = 3.7327 (11) Å] between the dihydropyrazole ring and the 4-methoxyphenyl ring link the molecules into centrosymmetric dimers. In addition, there are weak C—H···S, C—H···N and C—H···O interactions, which link the molecules into a complex three-dimensional array.

3D view



Chemical scheme



Structure description

Pyrazoles and thiazoles are important scaffolds for developing target drug molecules and exhibit a variety of pharmacological activities including antibacterial (Tanitame *et al.*, 2004), antifungal (Hassan, 2013), anti-inflammatory (Farghaly *et al.*, 2000), antidepressant (Secci *et al.*, 2011), antianalgesic (Jamwal *et al.*, 2013), anticancer (Keter & Darkwa, 2012), anitubercular (Kumar *et al.*, 2020), antiviral (Rashad *et al.*, 2008) and antidiabetic activity (Datar & Jadhav, 2013). The design, efficient synthesis and molecular docking of some thiazolyl-pyrazole derivatives as anticancer reagents have been reported (Sayed *et al.*, 2019). We have recently reported the formation of 1-(thiazol-2-yl)-4,5-dihydropyrazoles from simple precursors: synthesis, spectroscopic characterization and the

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

D—H···A	D—H	H···A	D···A	D—H···A
C20—H20A···S1^{i}	0.98	2.96	3.642 (2)	128
C23—H23A···N3^{ii}	0.95	2.59	3.490 (2)	159

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

structures of an intermediate and two products (Mahesha *et al.*, 2021). A series of 1,3-thiazole integrated pyrazoline scaffolds have been synthesized and characterized (CSD refcodes DADQIL, DADQEH; Salian *et al.*, 2017). The synthesis, fluorescence, TGA and crystal structure of a thiazolyl-pyrazoline derived from chalcones has been described (JUNRAN; Suwunwong *et al.*, 2015). In addition, the following crystal structures of related compounds have been reported: 2-[3-(4-bromophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]-4-phenyl-1,3-thiazole (IDOMOF; Abdel-Wahab *et al.*, 2013*c*), 2-[5-(4-fluorophenyl)-3-(4-methylphenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]-4-phenyl-1,3-thiazol (MEWQUC; Abdel-Wahab *et al.*, 2013*a*), 2-[3-(4-chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]-4-phenyl-1,3-thiazole (WIGQIO; Abdel-Wahab *et al.*, 2013*b*), 2-[3-(4-chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]-8*H*-indeno[1,2-*d*]thiazole (WOCFEC; El-Hiti *et al.*, 2019) and 2-[3-(4-bromophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]-8*H*-indeno[1,2-*d*]thiazole (PUVVAG; Alotaibi *et al.*, 2020).

With this in mind, the present study was planned to synthesize a ring system that contains both pyrazole and thiazole in a single molecule with an acetylene substituent, which can further be modified into highly functionalized heterocycles (Larock & Yum, 1991; Sonogashira, 2002). A related molecule, **4**, [5-(4-fluorophenyl)-1-[4-(4-methylphenyl)thiazol-2-yl]-3-[4-(prop-2-ynyloxy)phenyl]-4,5-dihydro-1*H*-pyrazole] has been published recently (Archana *et al.*, 2022). This paper reports the synthesis and crystal structure of the title compound, $C_{29}H_{25}N_3O_3S$, (**3**), which crystallizes in the monoclinic space group, $P2_1/n$, with four molecules in the asymmetric unit. In order to assist the discussion, the rings are labeled as C7–C12 (*A*), C4–C6/N3/S1 (*B*), C1–C3/N1/N2 (*C*), C21–C26 (*D*), and the major component of the disordered 4-methoxyphenyl ring, C14–C19 (*E*). Ring *E* is disordered

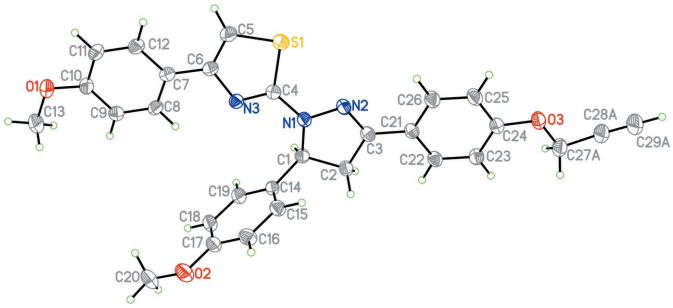


Figure 1
The major occupancy component of the title compound with atom labeling. Atomic displacement parameters are drawn at the 30% probability level.

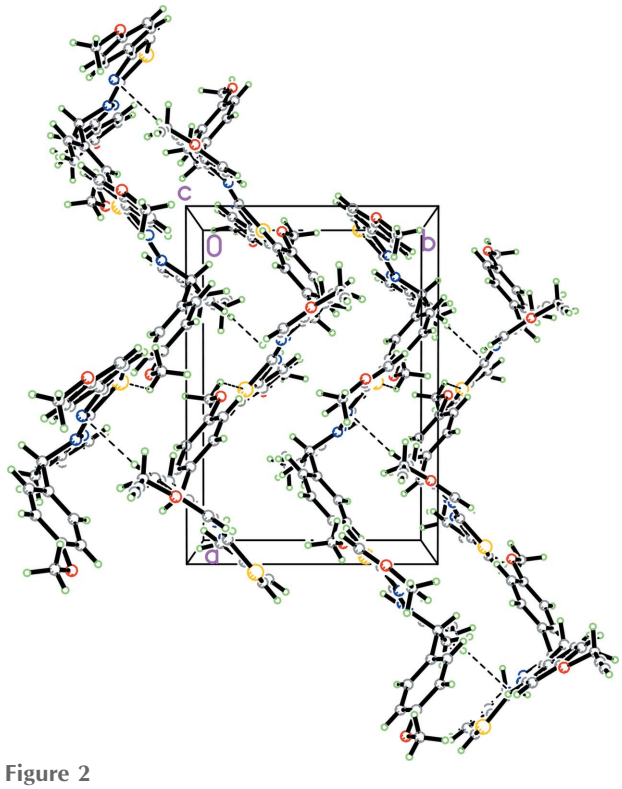


Figure 2
Packing diagram for **3** viewed along the *c* axis. C—H···N intermolecular interactions are shown as dashed lines.

over two equivalent conformations with occupancies of 0.903 (2):0.097 (2) and the two components are slightly twisted with respect to each other [dihedral angle of 2.3 (9)°]. The prop-2-ynyloxy substituent on ring *D* is also disordered over two equivalent conformations with occupancies of 0.776 (5) and 0.224 (5) (see Fig. 1). The central four-ring system (rings *A*–*D*) is almost planar [dihedral angles between *A* and *B*, *B* and *C* and *C* and *D* of 13.1 (1), 10.9 (1) and 4.6 (1)°, respectively]. These dihedral angles are not cumulative as the dihedral angle between the two terminal rings, *A* and *D*, is 3.1 (1)°. Interestingly and similar to the structure of **4**, ring *C*, which contains two sp^3 carbon atoms, C1 and C2, is close to planar with an r.m.s. deviation from planarity of only 0.044 (1) Å. One reason (or consequence) of this planarity is that it minimizes steric repulsion between the H atoms attached to C2 and H22*A* attached to C22 of the adjacent ring *D*. As would be expected, the dihedral angle between rings *C* and *E* is close to 90 [88.44 (6)°]. As in structure **4**, there are π–π interactions between rings *A* and *C*, which link the molecules into centrosymmetric dimers [centroid–centroid distance = 3.7327 (11) Å, with a slippage of 1.275 Å]. In addition, there are weak C—H···S and C—H···N interactions, which link the molecules into a complex three-dimensional array (see Table 1, Fig. 2).

Synthesis and crystallization

1-(*p*-Propyloxyphenyl)-3-(*p*-fluorophenyl)prop-2-ene-1-one (**1**) was obtained by the base-catalyzed condensation of *p*-

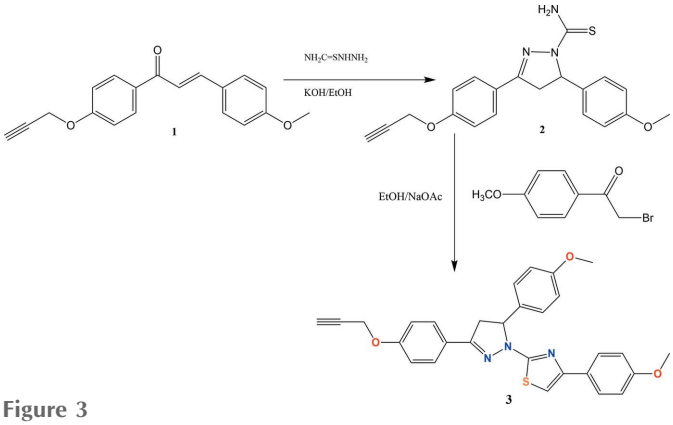


Figure 3
Reaction scheme showing the synthesis of the title compound **3**.

propylyoxyacetophenone with *p*-fluorobenazaldehyde in an ethanol medium employing sodium hydroxide as catalyst. This propenone (**1**) upon treatment with thiosemicarbazide in alcoholic potassium hydroxide gave compound (**2**).

4,5-Dihydro-3-(4-methoxyphenyl)-5-[4-(prop-2-ynyloxy)-phenyl]pyrazole-1-carbothioamide (**2**) (1 g, 0.002 mol) in ethanol (20 ml), 4-methoxyphenacyl bromide (0.5 g, 0.002 mol) and sodium acetate (0.162 g, 0.002 mol) were heated at reflux for 1 h. After cooling, the obtained product was collected by filtration and crystallized from the mixed solvents of ethanol and DMF (3:2). The reaction scheme shown in Fig. 3. Yield: 84%, m.p.: 486–488 K. Analysis for $C_{29}H_{25}N_3O_3S$, MS (*m*/*z*) 496 (M^+ + 1). ^{1}H NMR (400 MHz, $CDCl_3$, δ p.p.m.): 2.542 (*s*, 1*H*, triple bonded C—H), 3.25 (*dd*, 1*H*, J_{AX} = 17.2 Hz and J_{AB} = 6.4 Hz), 3.77 (*s*, 2H, OCH_3), 3.80 (*s*, 3H, OCH_3), 3.81 (*dd*, 1H, J_{XA} = 17.2 Hz and J_{XB} = 5.2 Hz), 4.738 (*s*, 2H, O—CH_2), 5.60 (*dd*, 1*H*, J_{BA} = 6.8 Hz and J_{BX} = 12.0 Hz), 6.651 (*s*, 1H), 6.84 (*m*, 4H, Ar—H), 7.01 (*dd*, 2H, *J* = 8.8 Hz, Ar—H), 7.34 (*dd*, 2H, *J* = 8.4 Hz, Ar—H), 7.61(*dd*, 2H, *J* = 8.8 Hz, Ar—H), 7.71 (*dd*, 2H, *J* = 8.8 Hz, Ar—H).

Refinement

Crystal data, data collection and structure refinement details for **3** are summarized in Table 2. Both the 4-methoxyphenyl and the 4-prop-2-ynyloxy groups were found to be disordered over two conformations with occupancies of 0.903 (2)/0.097 (2) and 0.776 (5)/0.224 (5), respectively.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{29}H_{25}N_3O_3S$
M_r	495.58
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, *b*, *c* (Å)	13.9677 (11), 9.7997 (5), 18.4125 (14)
β (°)	92.980 (3)
V (Å^3)	2516.9 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.17
Crystal size (mm)	0.37 × 0.28 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.687, 0.743
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38138, 6228, 4412
R_{int}	0.057
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.153, 1.05
No. of reflections	6228
No. of parameters	405
No. of restraints	373
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.35

Computer programs: *APEX2* (Bruker, 2005), *SAINT* (Bruker, 2002), SHELXT (Sheldrick 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *SHELXTL* (Sheldrick 2008).

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full crystallographic data

IUCrData (2022). **7**, x221047 [https://doi.org/10.1107/S2414314622010471]

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5-(4-Methoxyphenyl)-1-[4-(4-methoxyphenyl)thiazol-2-yl]-3-[4-(prop-2-ynyloxy)phenyl]-4,5-dihydro-1*H*-pyrazole

Crystal data

$C_{29}H_{25}N_3O_3S$
M_r = 495.58
Monoclinic, $P2_1/n$
a = 13.9677 (11) Å
b = 9.7997 (5) Å
c = 18.4125 (14) Å
β = 92.980 (3)°
V = 2516.9 (3) Å^3
Z = 4
$F(000)$ = 1040
D_x = 1.308 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8545 reflections
θ = 2.2–27.5°
μ = 0.17 mm^{-1}
T = 100 K
Prism, yellow-orange
0.37 × 0.28 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.687, T_{max} = 0.743
38138 measured reflections
6228 independent reflections
4412 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 28.3°, θ_{min} = 2.4°
h = −18→18
k = −10→13
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.153
S = 1.05
6228 reflections
405 parameters
373 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.8521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e 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. All hydrogen atoms were placed geometrically and refined as riding atoms with their U_{iso} values 1.2 times that of their attached atoms (1.5 times for CH_3 groups).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.48897 (4)	0.77965 (6)	0.35477 (3)	0.05560 (16)	
O1	0.48046 (12)	0.71860 (17)	0.79512 (8)	0.0688 (4)	
O3	0.71638 (11)	0.50421 (15)	−0.05972 (7)	0.0580 (4)	
N1	0.64253 (11)	0.61143 (15)	0.34811 (8)	0.0419 (3)	
N2	0.63262 (11)	0.62808 (14)	0.27352 (8)	0.0418 (3)	
N3	0.57829 (10)	0.65183 (14)	0.46069 (8)	0.0394 (3)	
C1	0.70011 (13)	0.48893 (17)	0.37091 (9)	0.0408 (4)	
H1A	0.656212	0.415582	0.387049	0.049*	
C2	0.74028 (14)	0.44839 (19)	0.29771 (9)	0.0445 (4)	
H2A	0.810217	0.464927	0.297907	0.053*	
H2B	0.727491	0.351023	0.286636	0.053*	
C3	0.68676 (13)	0.54007 (17)	0.24351 (9)	0.0406 (4)	
C4	0.57693 (12)	0.66946 (17)	0.39064 (9)	0.0391 (4)	
C5	0.45341 (15)	0.8047 (2)	0.44223 (11)	0.0550 (5)	
H5A	0.402316	0.862735	0.454685	0.066*	
C6	0.50804 (13)	0.73061 (17)	0.49073 (10)	0.0420 (4)	
C7	0.50199 (12)	0.72744 (17)	0.57007 (10)	0.0412 (4)	
C8	0.55106 (13)	0.62850 (18)	0.61154 (10)	0.0449 (4)	
H8A	0.588689	0.563153	0.587729	0.054*	
C9	0.54668 (14)	0.62246 (19)	0.68636 (10)	0.0486 (4)	
H9A	0.581093	0.554079	0.713367	0.058*	
C10	0.49168 (14)	0.7170 (2)	0.72161 (10)	0.0501 (4)	
C11	0.44338 (15)	0.8183 (2)	0.68139 (11)	0.0533 (5)	
H11A	0.406665	0.884324	0.705488	0.064*	
C12	0.44837 (14)	0.82349 (19)	0.60720 (11)	0.0486 (4)	
H12A	0.414977	0.893304	0.580556	0.058*	
C13	0.5360 (2)	0.6235 (3)	0.83832 (12)	0.0809 (8)	
H13A	0.520380	0.632679	0.889376	0.121*	
H13B	0.604304	0.641978	0.833629	0.121*	
H13C	0.521258	0.530507	0.821611	0.121*	
O2	0.96938 (12)	0.63122 (18)	0.60184 (9)	0.0653 (5)	0.9031 (18)
C14	0.77537 (9)	0.52104 (14)	0.43282 (6)	0.0390 (4)	0.9031 (18)
C15	0.84871 (10)	0.61382 (15)	0.42253 (6)	0.0475 (5)	0.9031 (18)
H15A	0.854884	0.654687	0.376226	0.057*	0.9031 (18)
C16	0.91302 (9)	0.64680 (15)	0.48000 (7)	0.0531 (5)	0.9031 (18)
H16A	0.963144	0.710213	0.472969	0.064*	0.9031 (18)
C17	0.90399 (10)	0.58700 (15)	0.54776 (6)	0.0490 (5)	0.9031 (18)

C18	0.83065 (11)	0.49422 (15)	0.55805 (5)	0.0501 (5)	0.9031 (18)
H18A	0.824483	0.453354	0.604357	0.060*	0.9031 (18)
C19	0.76634 (9)	0.46124 (13)	0.50058 (7)	0.0463 (4)	0.9031 (18)
H19A	0.716222	0.397826	0.507615	0.056*	0.9031 (18)
C20	0.9610 (2)	0.5818 (3)	0.67135 (12)	0.0777 (8)	0.9031 (18)
H20A	1.010049	0.623856	0.704115	0.117*	0.9031 (18)
H20B	0.969662	0.482600	0.671442	0.117*	0.9031 (18)
H20C	0.897241	0.603953	0.687890	0.117*	0.9031 (18)
O2A	0.9164 (9)	0.5416 (13)	0.6245 (4)	0.0582 (13)	0.0969 (18)
C14A	0.7577 (9)	0.4962 (15)	0.4289 (4)	0.0432 (12)	0.0969 (18)
C15A	0.8359 (10)	0.5840 (14)	0.4354 (5)	0.0453 (11)	0.0969 (18)
H15B	0.852659	0.637862	0.395113	0.054*	0.0969 (18)
C16A	0.8895 (9)	0.5930 (14)	0.5010 (5)	0.0489 (11)	0.0969 (18)
H16B	0.942930	0.652944	0.505490	0.059*	0.0969 (18)
C17A	0.8650 (9)	0.5142 (14)	0.5600 (4)	0.0505 (11)	0.0969 (18)
C18A	0.7868 (9)	0.4264 (13)	0.5534 (5)	0.0479 (13)	0.0969 (18)
H18B	0.770080	0.372543	0.593724	0.057*	0.0969 (18)
C19A	0.7332 (8)	0.4174 (14)	0.4878 (6)	0.0459 (12)	0.0969 (18)
H19B	0.679808	0.357460	0.483347	0.055*	0.0969 (18)
C20A	0.9051 (19)	0.460 (2)	0.6841 (6)	0.082 (3)	0.0969 (18)
H20D	0.962533	0.403490	0.692864	0.123*	0.0969 (18)
H20E	0.849170	0.400739	0.675099	0.123*	0.0969 (18)
H20F	0.895649	0.517020	0.726775	0.123*	0.0969 (18)
C21	0.69613 (13)	0.53308 (17)	0.16510 (9)	0.0402 (4)	
C22	0.74989 (14)	0.42971 (18)	0.13576 (10)	0.0442 (4)	
H22A	0.781885	0.366216	0.167561	0.053*	
C23	0.75834 (14)	0.41626 (18)	0.06136 (10)	0.0467 (4)	
H23A	0.795108	0.343945	0.042691	0.056*	
C24	0.71301 (14)	0.50857 (19)	0.01473 (10)	0.0450 (4)	
C25	0.66104 (16)	0.6156 (2)	0.04303 (11)	0.0541 (5)	
H25A	0.631401	0.680960	0.011091	0.065*	
C26	0.65219 (16)	0.6276 (2)	0.11689 (10)	0.0524 (5)	
H26A	0.615940	0.700623	0.135363	0.063*	
C27A	0.7636 (6)	0.3881 (8)	−0.08931 (18)	0.0595 (7)	0.776 (5)
H27A	0.739898	0.303503	−0.066937	0.071*	0.776 (5)
H27B	0.833461	0.394482	−0.077831	0.071*	0.776 (5)
C28A	0.7450 (3)	0.3823 (4)	−0.16871 (16)	0.0668 (8)	0.776 (5)
C29A	0.7342 (3)	0.3741 (5)	−0.23140 (18)	0.0949 (13)	0.776 (5)
H29A	0.725292	0.367315	−0.282778	0.114*	0.776 (5)
C27B	0.760 (2)	0.389 (3)	−0.0900 (5)	0.0633 (15)	0.224 (5)
H27C	0.717276	0.307691	−0.089321	0.076*	0.224 (5)
H27D	0.821888	0.366756	−0.064344	0.076*	0.224 (5)
C28B	0.7724 (10)	0.4367 (14)	−0.1646 (4)	0.0670 (15)	0.224 (5)
C29B	0.7878 (11)	0.4729 (16)	−0.2228 (5)	0.089 (2)	0.224 (5)
H29B	0.800357	0.502657	−0.270433	0.107*	0.224 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0604 (3)	0.0595 (3)	0.0466 (3)	0.0194 (2)	0.0006 (2)	0.0083 (2)
O1	0.0788 (11)	0.0863 (11)	0.0411 (8)	0.0198 (9)	0.0030 (7)	−0.0116 (7)
O3	0.0703 (9)	0.0672 (9)	0.0365 (7)	0.0163 (7)	0.0031 (6)	0.0021 (6)
N1	0.0473 (8)	0.0432 (8)	0.0348 (7)	0.0073 (6)	−0.0008 (6)	0.0003 (6)
N2	0.0480 (8)	0.0412 (7)	0.0357 (7)	0.0014 (6)	−0.0023 (6)	0.0000 (6)
N3	0.0393 (8)	0.0382 (7)	0.0406 (8)	0.0018 (6)	0.0017 (6)	−0.0013 (6)
C1	0.0434 (9)	0.0384 (8)	0.0406 (9)	0.0035 (7)	0.0015 (7)	0.0013 (7)
C2	0.0512 (10)	0.0452 (9)	0.0370 (9)	0.0064 (8)	0.0000 (8)	−0.0012 (7)
C3	0.0447 (9)	0.0370 (8)	0.0396 (9)	−0.0032 (7)	−0.0032 (7)	0.0001 (7)
C4	0.0385 (9)	0.0355 (8)	0.0430 (9)	−0.0006 (7)	−0.0002 (7)	−0.0007 (7)
C5	0.0560 (12)	0.0572 (11)	0.0523 (11)	0.0203 (9)	0.0065 (9)	0.0052 (9)
C6	0.0398 (9)	0.0375 (8)	0.0488 (10)	0.0031 (7)	0.0038 (7)	−0.0007 (7)
C7	0.0375 (9)	0.0381 (8)	0.0480 (10)	0.0000 (7)	0.0033 (7)	−0.0020 (7)
C8	0.0433 (10)	0.0440 (9)	0.0478 (10)	0.0074 (7)	0.0066 (8)	−0.0033 (7)
C9	0.0491 (10)	0.0495 (10)	0.0468 (10)	0.0083 (8)	−0.0009 (8)	−0.0011 (8)
C10	0.0504 (11)	0.0570 (11)	0.0430 (10)	0.0005 (9)	0.0022 (8)	−0.0091 (8)
C11	0.0538 (11)	0.0518 (10)	0.0545 (11)	0.0112 (9)	0.0051 (9)	−0.0133 (9)
C12	0.0495 (10)	0.0423 (9)	0.0540 (11)	0.0085 (8)	0.0026 (9)	−0.0045 (8)
C13	0.0922 (19)	0.107 (2)	0.0423 (12)	0.0244 (16)	−0.0058 (12)	−0.0021 (12)
O2	0.0609 (10)	0.0750 (11)	0.0582 (9)	−0.0034 (8)	−0.0138 (8)	−0.0081 (8)
C14	0.0414 (10)	0.0405 (9)	0.0350 (8)	0.0054 (8)	0.0014 (7)	−0.0004 (7)
C15	0.0459 (10)	0.0530 (11)	0.0433 (10)	−0.0013 (8)	−0.0003 (8)	0.0058 (8)
C16	0.0470 (11)	0.0566 (12)	0.0550 (11)	−0.0064 (9)	−0.0034 (9)	0.0027 (9)
C17	0.0489 (10)	0.0543 (10)	0.0427 (9)	0.0053 (8)	−0.0084 (8)	−0.0067 (8)
C18	0.0567 (11)	0.0570 (11)	0.0363 (9)	0.0042 (9)	−0.0013 (8)	0.0020 (8)
C19	0.0500 (10)	0.0489 (10)	0.0397 (9)	−0.0011 (8)	0.0010 (8)	0.0031 (8)
C20	0.0746 (17)	0.103 (2)	0.0528 (13)	0.0058 (15)	−0.0228 (12)	−0.0144 (13)
O2A	0.057 (2)	0.071 (2)	0.045 (2)	0.003 (2)	−0.011 (2)	−0.006 (2)
C14A	0.043 (2)	0.048 (2)	0.038 (2)	0.001 (2)	−0.001 (2)	0.001 (2)
C15A	0.046 (2)	0.049 (2)	0.041 (2)	−0.0004 (19)	−0.002 (2)	0.004 (2)
C16A	0.048 (2)	0.055 (2)	0.0433 (19)	−0.001 (2)	−0.0039 (19)	0.001 (2)
C17A	0.050 (2)	0.058 (2)	0.0418 (18)	0.0006 (19)	−0.0055 (19)	−0.0013 (19)
C18A	0.051 (3)	0.054 (3)	0.039 (2)	0.000 (2)	−0.003 (2)	0.002 (2)
C19A	0.049 (2)	0.050 (2)	0.038 (2)	0.000 (2)	−0.002 (2)	0.001 (2)
C20A	0.086 (7)	0.105 (7)	0.055 (5)	0.005 (7)	−0.012 (6)	0.006 (5)
C21	0.0445 (9)	0.0376 (8)	0.0381 (9)	−0.0030 (7)	−0.0015 (7)	0.0001 (7)
C22	0.0526 (10)	0.0396 (9)	0.0400 (9)	0.0040 (8)	−0.0007 (8)	0.0041 (7)
C23	0.0557 (11)	0.0413 (9)	0.0432 (10)	0.0044 (8)	0.0031 (8)	−0.0004 (7)
C24	0.0484 (10)	0.0483 (10)	0.0382 (9)	−0.0008 (8)	0.0004 (8)	0.0007 (7)
C25	0.0663 (13)	0.0536 (11)	0.0416 (10)	0.0142 (9)	−0.0037 (9)	0.0057 (8)
C26	0.0662 (13)	0.0485 (10)	0.0421 (10)	0.0138 (9)	−0.0009 (9)	−0.0003 (8)
C27A	0.0708 (17)	0.0651 (14)	0.0433 (12)	0.0111 (13)	0.0087 (12)	−0.0033 (12)
C28A	0.0751 (19)	0.0782 (19)	0.0477 (13)	0.0140 (15)	0.0078 (13)	−0.0069 (13)
C29A	0.105 (3)	0.130 (3)	0.0498 (16)	0.037 (2)	0.0049 (17)	−0.0135 (19)
C27B	0.074 (3)	0.072 (3)	0.045 (2)	0.013 (3)	0.008 (3)	−0.006 (3)

C28B	0.077 (3)	0.079 (3)	0.045 (2)	0.017 (3)	0.011 (2)	−0.007 (2)
C29B	0.102 (5)	0.117 (5)	0.050 (4)	0.019 (5)	0.016 (4)	0.004 (4)

Geometric parameters (Å, º)

S1—C5	1.727 (2)	C16—H16A	0.9500
S1—C4	1.7399 (18)	C17—C18	1.3900
O1—C10	1.371 (2)	C18—C19	1.3900
O1—C13	1.428 (3)	C18—H18A	0.9500
O3—C24	1.375 (2)	C19—H19A	0.9500
O3—C27B	1.41 (3)	C20—H20A	0.9800
O3—C27A	1.437 (8)	C20—H20B	0.9800
N1—C4	1.360 (2)	C20—H20C	0.9800
N1—N2	1.3829 (19)	O2A—C20A	1.374 (6)
N1—C1	1.493 (2)	O2A—C17A	1.382 (4)
N2—C3	1.290 (2)	C14A—C15A	1.3900
N3—C4	1.300 (2)	C14A—C19A	1.3900
N3—C6	1.386 (2)	C15A—C16A	1.3900
C1—C14A	1.305 (7)	C15A—H15B	0.9500
C1—C2	1.539 (2)	C16A—C17A	1.3900
C1—C14	1.5424 (19)	C16A—H16B	0.9500
C1—H1A	1.0000	C17A—C18A	1.3900
C2—C3	1.511 (2)	C18A—C19A	1.3900
C2—H2A	0.9900	C18A—H18B	0.9500
C2—H2B	0.9900	C19A—H19B	0.9500
C3—C21	1.458 (2)	C20A—H20D	0.9800
C5—C6	1.355 (3)	C20A—H20E	0.9800
C5—H5A	0.9500	C20A—H20F	0.9800
C6—C7	1.468 (3)	C21—C22	1.387 (2)
C7—C8	1.392 (2)	C21—C26	1.402 (2)
C7—C12	1.403 (2)	C22—C23	1.387 (2)
C8—C9	1.384 (3)	C22—H22A	0.9500
C8—H8A	0.9500	C23—C24	1.378 (3)
C9—C10	1.386 (3)	C23—H23A	0.9500
C9—H9A	0.9500	C24—C25	1.392 (3)
C10—C11	1.392 (3)	C25—C26	1.377 (3)
C11—C12	1.372 (3)	C25—H25A	0.9500
C11—H11A	0.9500	C26—H26A	0.9500
C12—H12A	0.9500	C27A—C28A	1.472 (4)
C13—H13A	0.9800	C27A—H27A	0.9900
C13—H13B	0.9800	C27A—H27B	0.9900
C13—H13C	0.9800	C28A—C29A	1.159 (4)
O2—C20	1.379 (3)	C29A—H29A	0.9500
O2—C17	1.3852 (17)	C27B—C28B	1.473 (6)
C14—C15	1.3900	C27B—H27C	0.9900
C14—C19	1.3900	C27B—H27D	0.9900
C15—C16	1.3900	C28B—C29B	1.159 (5)
C15—H15A	0.9500	C29B—H29B	0.9500

C16—C17	1.3900

C5—S1—C4	88.05 (9)	C17—C18—C19	120.0
C10—O1—C13	117.13 (17)	C17—C18—H18A	120.0
C24—O3—C27B	117.1 (5)	C19—C18—H18A	120.0
C24—O3—C27A	116.29 (19)	C18—C19—C14	120.0
C4—N1—N2	119.12 (14)	C18—C19—H19A	120.0
C4—N1—C1	122.91 (14)	C14—C19—H19A	120.0
N2—N1—C1	113.50 (13)	O2—C20—H20A	109.5
C3—N2—N1	108.41 (14)	O2—C20—H20B	109.5
C4—N3—C6	110.35 (15)	H20A—C20—H20B	109.5
C14A—C1—N1	119.1 (7)	O2—C20—H20C	109.5
C14A—C1—C2	119.5 (6)	H20A—C20—H20C	109.5
N1—C1—C2	100.19 (13)	H20B—C20—H20C	109.5
N1—C1—C14	112.35 (13)	C20A—O2A—C17A	119.8 (8)
C2—C1—C14	115.75 (14)	C1—C14A—C15A	123.6 (8)
N1—C1—H1A	109.4	C1—C14A—C19A	116.2 (8)
C2—C1—H1A	109.4	C15A—C14A—C19A	120.0
C14—C1—H1A	109.4	C16A—C15A—C14A	120.0
C3—C2—C1	103.56 (14)	C16A—C15A—H15B	120.0
C3—C2—H2A	111.0	C14A—C15A—H15B	120.0
C1—C2—H2A	111.0	C15A—C16A—C17A	120.0
C3—C2—H2B	111.0	C15A—C16A—H16B	120.0
C1—C2—H2B	111.0	C17A—C16A—H16B	120.0
H2A—C2—H2B	109.0	O2A—C17A—C16A	115.2 (5)
N2—C3—C21	122.71 (15)	O2A—C17A—C18A	124.5 (5)
N2—C3—C2	113.29 (15)	C16A—C17A—C18A	120.0
C21—C3—C2	123.99 (15)	C19A—C18A—C17A	120.0
N3—C4—N1	122.67 (16)	C19A—C18A—H18B	120.0
N3—C4—S1	115.63 (13)	C17A—C18A—H18B	120.0
N1—C4—S1	121.63 (13)	C18A—C19A—C14A	120.0
C6—C5—S1	111.04 (15)	C18A—C19A—H19B	120.0
C6—C5—H5A	124.5	C14A—C19A—H19B	120.0
S1—C5—H5A	124.5	O2A—C20A—H20D	109.5
C5—C6—N3	114.93 (17)	O2A—C20A—H20E	109.5
C5—C6—C7	127.42 (17)	H20D—C20A—H20E	109.5
N3—C6—C7	117.64 (15)	O2A—C20A—H20F	109.5
C8—C7—C12	117.40 (17)	H20D—C20A—H20F	109.5
C8—C7—C6	120.55 (16)	H20E—C20A—H20F	109.5
C12—C7—C6	122.05 (16)	C22—C21—C26	117.63 (17)
C9—C8—C7	122.00 (16)	C22—C21—C3	119.89 (15)
C9—C8—H8A	119.0	C26—C21—C3	122.48 (16)
C7—C8—H8A	119.0	C23—C22—C21	121.97 (16)
C8—C9—C10	119.47 (17)	C23—C22—H22A	119.0
C8—C9—H9A	120.3	C21—C22—H22A	119.0
C10—C9—H9A	120.3	C24—C23—C22	119.53 (17)
O1—C10—C9	124.39 (18)	C24—C23—H23A	120.2
O1—C10—C11	116.10 (17)	C22—C23—H23A	120.2

C9—C10—C11	119.51 (18)	O3—C24—C23	124.22 (17)
C12—C11—C10	120.53 (17)	O3—C24—C25	116.25 (16)
C12—C11—H11A	119.7	C23—C24—C25	119.52 (17)
C10—C11—H11A	119.7	C26—C25—C24	120.63 (17)
C11—C12—C7	121.07 (18)	C26—C25—H25A	119.7
C11—C12—H12A	119.5	C24—C25—H25A	119.7
C7—C12—H12A	119.5	C25—C26—C21	120.67 (18)
O1—C13—H13A	109.5	C25—C26—H26A	119.7
O1—C13—H13B	109.5	C21—C26—H26A	119.7
H13A—C13—H13B	109.5	O3—C27A—C28A	110.3 (5)
O1—C13—H13C	109.5	O3—C27A—H27A	109.6
H13A—C13—H13C	109.5	C28A—C27A—H27A	109.6
H13B—C13—H13C	109.5	O3—C27A—H27B	109.6
C20—O2—C17	118.21 (19)	C28A—C27A—H27B	109.6
C15—C14—C19	120.0	H27A—C27A—H27B	108.1
C15—C14—C1	120.76 (10)	C29A—C28A—C27A	176.8 (5)
C19—C14—C1	119.16 (10)	C28A—C29A—H29A	180.0
C16—C15—C14	120.0	O3—C27B—C28B	100.7 (15)
C16—C15—H15A	120.0	O3—C27B—H27C	111.6
C14—C15—H15A	120.0	C28B—C27B—H27C	111.6
C17—C16—C15	120.0	O3—C27B—H27D	111.6
C17—C16—H16A	120.0	C28B—C27B—H27D	111.6
C15—C16—H16A	120.0	H27C—C27B—H27D	109.4
O2—C17—C16	115.22 (12)	C29B—C28B—C27B	176.2 (19)
O2—C17—C18	124.73 (12)	C28B—C29B—H29B	180.0
C16—C17—C18	120.0		

C4—N1—N2—C3	−164.73 (16)	C19—C14—C15—C16	0.0
C1—N1—N2—C3	−7.73 (19)	C1—C14—C15—C16	176.71 (14)
C4—N1—C1—C14A	−61.3 (7)	C14—C15—C16—C17	0.0
N2—N1—C1—C14A	142.7 (7)	C20—O2—C17—C16	176.35 (18)
C4—N1—C1—C2	166.41 (16)	C20—O2—C17—C18	−1.0 (3)
N2—N1—C1—C2	10.40 (18)	C15—C16—C17—O2	−177.48 (14)
C4—N1—C1—C14	−70.1 (2)	C15—C16—C17—C18	0.0
N2—N1—C1—C14	133.85 (14)	O2—C17—C18—C19	177.23 (16)
C14A—C1—C2—C3	−140.7 (7)	C16—C17—C18—C19	0.0
N1—C1—C2—C3	−8.68 (17)	C17—C18—C19—C14	0.0
C14—C1—C2—C3	−129.73 (15)	C15—C14—C19—C18	0.0
N1—N2—C3—C21	−177.66 (15)	C1—C14—C19—C18	−176.76 (13)
N1—N2—C3—C2	1.1 (2)	N1—C1—C14A—C15A	−62.8 (10)
C1—C2—C3—N2	5.4 (2)	C2—C1—C14A—C15A	60.5 (11)
C1—C2—C3—C21	−175.90 (16)	N1—C1—C14A—C19A	112.5 (7)
C6—N3—C4—N1	175.47 (16)	C2—C1—C14A—C19A	−124.2 (7)
C6—N3—C4—S1	−1.41 (19)	C1—C14A—C15A—C16A	175.1 (13)
N2—N1—C4—N3	175.93 (15)	C19A—C14A—C15A—C16A	0.0
C1—N1—C4—N3	21.2 (3)	C14A—C15A—C16A—C17A	0.0
N2—N1—C4—S1	−7.4 (2)	C20A—O2A—C17A—C16A	−173.0 (16)
C1—N1—C4—S1	−162.11 (13)	C20A—O2A—C17A—C18A	14 (2)

C5—S1—C4—N3	0.97 (15)	C15A—C16A—C17A—O2A	−173.4 (13)
C5—S1—C4—N1	−175.95 (16)	C15A—C16A—C17A—C18A	0.0
C4—S1—C5—C6	−0.22 (16)	O2A—C17A—C18A—C19A	172.7 (14)
S1—C5—C6—N3	−0.5 (2)	C16A—C17A—C18A—C19A	0.0
S1—C5—C6—C7	178.12 (15)	C17A—C18A—C19A—C14A	0.0
C4—N3—C6—C5	1.2 (2)	C1—C14A—C19A—C18A	−175.5 (12)
C4—N3—C6—C7	−177.54 (15)	C15A—C14A—C19A—C18A	0.0
C5—C6—C7—C8	168.4 (2)	N2—C3—C21—C22	−175.21 (17)
N3—C6—C7—C8	−13.0 (2)	C2—C3—C21—C22	6.2 (3)
C5—C6—C7—C12	−12.4 (3)	N2—C3—C21—C26	4.6 (3)
N3—C6—C7—C12	166.16 (17)	C2—C3—C21—C26	−174.07 (18)
C12—C7—C8—C9	1.0 (3)	C26—C21—C22—C23	−1.9 (3)
C6—C7—C8—C9	−179.83 (17)	C3—C21—C22—C23	177.88 (17)
C7—C8—C9—C10	0.3 (3)	C21—C22—C23—C24	0.6 (3)
C13—O1—C10—C9	5.6 (3)	C27B—O3—C24—C23	7.7 (14)
C13—O1—C10—C11	−174.6 (2)	C27A—O3—C24—C23	5.7 (4)
C8—C9—C10—O1	178.44 (18)	C27B—O3—C24—C25	−173.3 (13)
C8—C9—C10—C11	−1.4 (3)	C27A—O3—C24—C25	−175.3 (4)
O1—C10—C11—C12	−178.57 (19)	C22—C23—C24—O3	−179.70 (18)
C9—C10—C11—C12	1.3 (3)	C22—C23—C24—C25	1.3 (3)
C10—C11—C12—C7	0.0 (3)	O3—C24—C25—C26	178.99 (19)
C8—C7—C12—C11	−1.1 (3)	C23—C24—C25—C26	−2.0 (3)
C6—C7—C12—C11	179.72 (18)	C24—C25—C26—C21	0.7 (3)
N1—C1—C14—C15	−62.36 (16)	C22—C21—C26—C25	1.2 (3)
C2—C1—C14—C15	51.90 (17)	C3—C21—C26—C25	−178.52 (18)
N1—C1—C14—C19	114.38 (13)	C24—O3—C27A—C28A	168.6 (4)
C2—C1—C14—C19	−131.37 (13)	C24—O3—C27B—C28B	−165.9 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H20*A*···S1^{i}	0.98	2.96	3.642 (2)	128
C20*A*—H20*D*···O1^{ii}	0.98	1.99	2.87 (2)	148
C23—H23*A*···N3^{iii}	0.95	2.59	3.490 (2)	159

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