IUCrData

ISSN 2414-3146

3-(2-Hydroxy-4-methoxyphenyl)-*N*-(2-methoxyphenyl)-5-(naphthalen-1-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

Seunghyun Ahn,[a] Yoongho Lim,[a] Jiha Sung[b] and Dongsoo Koh[b]*

[a]Division of Bioscience and Biotechnology, BMIC, Konkuk University, Seoul 143-701, Republic of Korea, and [b]Department of Applied Chemistry, Dongduk Women's University, Seoul 136-714, Republic of Korea. *Correspondence e-mail: dskoh@dongduk.ac.kr

Received 7 May 2017
Accepted 17 May 2017

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

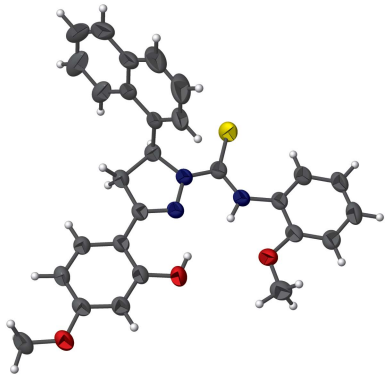
Keywords: crystal structure; pyrazoline; thioamide.

CCDC reference: 1550731

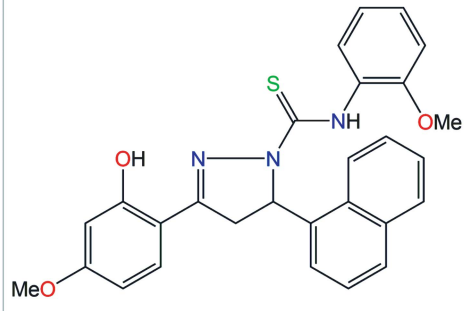
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{28}H_{25}N_3O_3S$, the dihedral angles formed by the naphthalene ring system and the benzene rings are 73.03 (13) and 74.04 (11)°. The benzene rings attached to the central pyrazoline ring are almost coplanar, as indicated by the dihedral angle of 2.22 (10)° between them. The C atom of the methoxy group of the phenol ring is essentially coplanar with the ring [C—C—O—C = −0.3 (3)°], whereas the C atom of the methoxy group of the thioamide benzene ring is slightly twisted [C—C—O—C = 5.4 (3)°]. An intramolecular O—H···N hydrogen bond generates an $S(6)$ ring motif. In the crystal, pairs of very weak C—H···S interactions form inversion dimers with an $R_2^2(18)$ motif.

3D view



Chemical scheme



Structure description

Pyrazolines show a broad spectrum of biological activities including the dual function of antimalarial and antimicrobial (Mishra, *et al.*, 2017), antibacterial (Viveka *et al.*, 2015), anti-inflammatory (Kharbanda, *et al.*, 2014) and antitumor activities (Bashir *et al.*, 2011). In continuation of our studies of new pyrazoline derivatives which may show broad range of biological activities (Jung *et al.* 2015), the title compound **I** was synthesized and its crystal structure was determined. For related structures, see: Abdel-Wahab *et al.* (2013); Koh *et al.* (2014).

The molecular structure of **I** is shown in Fig. 1. The benzene ring and naphthalene ring system are attached at the C1 and C3 position of central pyrazoline ring and another benzene ring is attached at N1 by a carbothioamide linkage. The dihedral angles formed by the naphthalene ring system at C3 and the benzene rings at C1 and N1 are 73.03 (13) and 74.04 (11)°, respectively. The benzene rings attached to the pyrazoline ring at C1 and

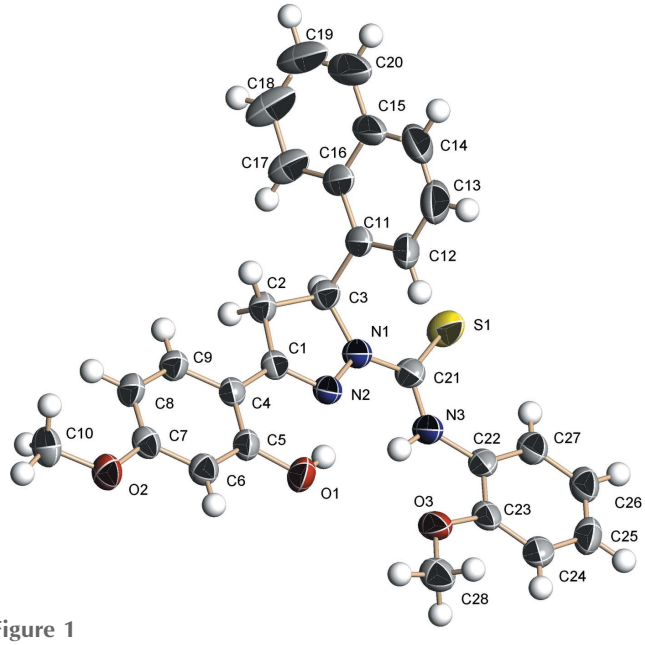


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level

N1 are almost in the same plane [dihedral angle = 2.22 (10)°]. The C atom of the methoxy group of the phenol ring is essentially co-planar with the ring [C8—C7—O2—C10 = −0.3 (3)°], whereas the C atom of the methoxy group at the thioamide benzene ring is slightly twisted from the ring plane [C24—C23—O3—C28 = 5.4 (3)°]. An intramolecular O1—H1*O*···N1 hydrogen bond forms an *S*(6) ring motif (Table 1). In the crystal, pairs of week C—H···S interactions form inversion dimers (Fig. 2).

Synthesis and crystallization

By the previously reported method (Jung *et al.* 2015), chalcone intermediate **III** was prepared and converted into pyrazoline intermediate **IV** *via* imine formation followed by Michael addition of hydrazine. The reaction between **IV** and isothiocyanate **V** gave the desired pyrazoline carbothiamide (see Fig. 3).

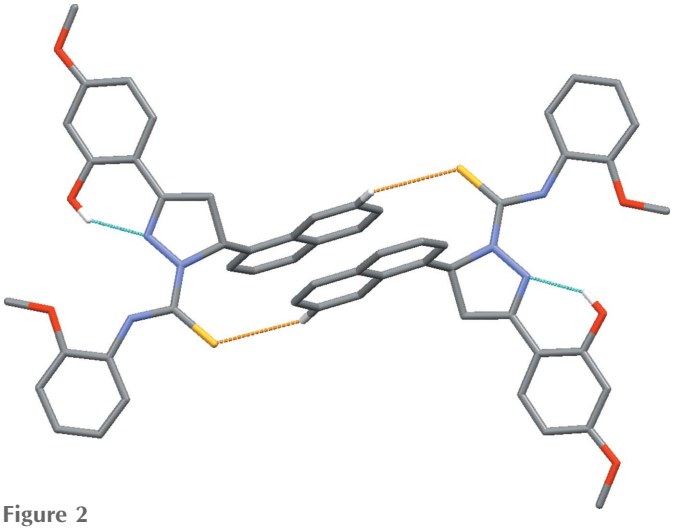


Figure 2
A view of an inversion dimer formed by a pair of C—H···S interactions in the crystal structure of the title compound.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.84	1.96	2.6889 (19)	145
C18—H18···S1^{i}	0.95	2.96	3.712 (2)	137

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{28}H_{25}N_3O_3S$
M_r	483.57
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, *b*, *c* (Å)	6.8521 (4), 23.1503 (13), 15.0422 (8)
β (°)	99.365 (1)
V (Å^3)	2354.3 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.17
Crystal size (mm)	0.22 × 0.16 × 0.10
Data collection	
Diffractometer	Bruker SMART CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17230, 5827, 3091
R_{int}	0.044
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.147, 0.96
No. of reflections	5827
No. of parameters	319
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.24

Computer programs: *SMART* and *SAINT* (Bruker, 2000) and *SHELXTL* (Sheldrick, 2008).

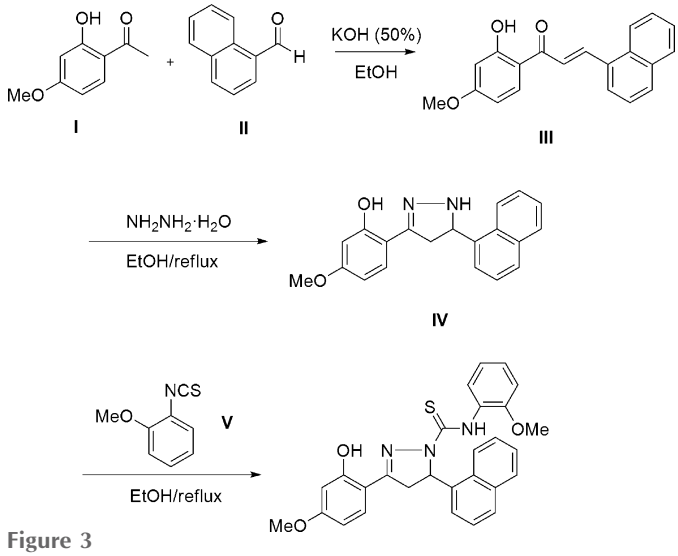


Figure 3
The synthetic procedure for the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

Funding for this research was provided by: the Basic Science Research Program (award No. NRF-2016R1D1A1B03931623).

References

Abdel-Wahab, B. F., Ng, S. W. & Tiekink, E. R. T. (2013). *Acta Cryst.* E**69**, o619.

Bashir, R., Ovais, S., Yaseen, S., Hamid, H., Alam, M. S., Samim, M., Singh, S. & Javed, K. (2011). *Bioorg. Med. Chem. Lett.* **21**, 4301–4305.

Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Jung, H., Ahn, S., Park, M., Yoon, H., Noh, H. J., Kim, S. Y., Yoo, J. S., Koh, D. & Lim, Y. (2015). *Magn. Reson. Chem.* **53**, 383–390.

Kharbanda, C., Alam, M. S., Hamid, H., Javed, K., Bano, B., Dhulap, A., Ali, Y., Nazreen, S. & Haider, S. (2014). *Bioorg. Med. Chem.* **22**, 5804–5812.

Koh, D., Lim, Y. & Lough, A. J. (2014). *Acta Cryst.* E**70**, o464.

Mishra, V. K., Mishra, M., Kashaw, V. & Kashaw, S. K. (2017). *Bioorg. Med. Chem.* **25**, 1949–1962.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Viveka, S., Dinesha, Shama, P., Nagaraja, G. K., Ballav, S. & Kerkar, S. (2015). *Eur. J. Med. Chem.* **101**, 442–451.

full crystallographic data

IUCrData (2017). **2**, x170732 [https://doi.org/10.1107/S2414314617007325]

3-(2-Hydroxy-4-methoxyphenyl)-*N*-(2-methoxyphenyl)-5-(naphthalen-1-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

Seunghyun Ahn, Yoongho Lim, Jiha Sung and Dongsoo Koh

3-(2-Hydroxy-4-methoxyphenyl)-*N*-(2-methoxyphenyl)-5-(naphthalen-1-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

Crystal data

$C_{28}H_{25}N_3O_3S$
M_r = 483.57
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 6.8521 (4) Å
b = 23.1503 (13) Å
c = 15.0422 (8) Å
β = 99.365 (1)°
V = 2354.3 (2) Å^3
Z = 4
$F(000)$ = 1016
D_x = 1.364 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5750 reflections
θ = 2.2–27.9°
μ = 0.17 mm^{-1}
T = 173 K
Block, yellow
0.22 × 0.16 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
17230 measured reflections
5827 independent reflections
3091 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 28.3°, θ_{min} = 1.8°
h = −8→9
k = −23→30
l = −20→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.147
S = 0.96
5827 reflections
319 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 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. 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 $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.6669 (2)	0.68425 (6)	0.92398 (10)	0.0466 (4)
N2	0.7136 (2)	0.74261 (6)	0.93947 (10)	0.0443 (4)
C1	0.8947 (3)	0.74602 (8)	0.98041 (11)	0.0405 (4)
C2	0.9924 (3)	0.68823 (7)	0.99689 (12)	0.0431 (4)
H2A	1.0532	0.6837	1.0609	0.052*
H2B	1.0951	0.6826	0.9584	0.052*
C3	0.8196 (3)	0.64595 (8)	0.97126 (12)	0.0437 (5)
H3	0.8551	0.6155	0.9296	0.052*
C4	0.9887 (3)	0.80096 (8)	1.00541 (12)	0.0406 (4)
C5	0.8889 (3)	0.85421 (8)	0.99168 (12)	0.0448 (5)
O1	0.69489 (19)	0.85814 (6)	0.95457 (10)	0.0583 (4)
H1	0.6497	0.8249	0.9416	0.087*
C6	0.9869 (3)	0.90568 (8)	1.01527 (13)	0.0478 (5)
H6	0.9175	0.9413	1.0064	0.057*
C7	1.1853 (3)	0.90539 (8)	1.05168 (12)	0.0457 (5)
C8	1.2875 (3)	0.85359 (8)	1.06688 (13)	0.0490 (5)
H8	1.4235	0.8533	1.0928	0.059*
C9	1.1890 (3)	0.80279 (8)	1.04382 (12)	0.0456 (5)
H9	1.2594	0.7675	1.0543	0.055*
O2	1.2692 (2)	0.95858 (5)	1.06886 (9)	0.0563 (4)
C10	1.4744 (3)	0.96092 (9)	1.10511 (15)	0.0614 (6)
H10A	1.4972	0.9425	1.1645	0.092*
H10B	1.5173	1.0013	1.1109	0.092*
H10C	1.5500	0.9406	1.0648	0.092*
C11	0.7552 (3)	0.61868 (8)	1.05338 (13)	0.0477 (5)
C12	0.5914 (3)	0.63734 (10)	1.08515 (15)	0.0646 (6)
H12	0.5114	0.6666	1.0533	0.078*
C13	0.5384 (4)	0.61442 (16)	1.1636 (2)	0.1038 (11)
H13	0.4251	0.6287	1.1855	0.125*
C14	0.6474 (5)	0.57218 (16)	1.2083 (2)	0.1130 (12)
H14	0.6082	0.5565	1.2611	0.136*
C15	0.8173 (4)	0.55059 (11)	1.17942 (17)	0.0820 (9)
C16	0.8761 (3)	0.57470 (8)	1.10030 (14)	0.0574 (6)
C17	1.0517 (4)	0.55469 (8)	1.07327 (16)	0.0678 (7)
H17	1.0942	0.5709	1.0217	0.081*

C18	1.1624 (5)	0.51184 (10)	1.1209 (2)	0.0945 (10)
H18	1.2799	0.4984	1.1018	0.113*
C19	1.1014 (6)	0.48799 (11)	1.1980 (2)	0.1073 (14)
H19	1.1788	0.4588	1.2312	0.129*
C20	0.9358 (6)	0.50619 (14)	1.2246 (2)	0.1161 (14)
H20	0.8958	0.4887	1.2759	0.139*
C21	0.4949 (3)	0.66760 (9)	0.87116 (12)	0.0486 (5)
S1	0.43887 (9)	0.59834 (2)	0.85550 (4)	0.0700 (2)
N3	0.3851 (2)	0.71315 (7)	0.83677 (11)	0.0572 (5)
H3A	0.4489	0.7463	0.8429	0.069*
C22	0.1887 (3)	0.71777 (9)	0.79305 (12)	0.0484 (5)
C23	0.1202 (3)	0.77489 (9)	0.78290 (12)	0.0491 (5)
C24	−0.0711 (3)	0.78644 (9)	0.74395 (13)	0.0547 (5)
H24	−0.1168	0.8252	0.7370	0.066*
C25	−0.1979 (3)	0.74061 (10)	0.71471 (14)	0.0604 (6)
H25	−0.3308	0.7482	0.6880	0.073*
C26	−0.1321 (3)	0.68513 (10)	0.72435 (13)	0.0584 (6)
H26	−0.2202	0.6543	0.7046	0.070*
C27	0.0604 (3)	0.67287 (9)	0.76234 (13)	0.0550 (5)
H27	0.1051	0.6340	0.7675	0.066*
O3	0.2590 (2)	0.81574 (6)	0.81542 (9)	0.0614 (4)
C28	0.1973 (3)	0.87432 (9)	0.81590 (14)	0.0618 (6)
H28A	0.1587	0.8878	0.7538	0.093*
H28B	0.3065	0.8981	0.8463	0.093*
H28C	0.0843	0.8775	0.8480	0.093*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0468 (10)	0.0413 (9)	0.0474 (9)	−0.0097 (7)	−0.0052 (7)	0.0015 (7)
N2	0.0457 (10)	0.0427 (9)	0.0416 (8)	−0.0089 (7)	−0.0018 (7)	0.0023 (7)
C1	0.0398 (11)	0.0484 (11)	0.0330 (9)	−0.0060 (8)	0.0049 (8)	−0.0007 (8)
C2	0.0391 (11)	0.0472 (11)	0.0425 (10)	−0.0044 (8)	0.0052 (8)	−0.0030 (8)
C3	0.0443 (12)	0.0426 (10)	0.0416 (10)	−0.0029 (8)	−0.0011 (8)	−0.0047 (8)
C4	0.0375 (10)	0.0453 (11)	0.0390 (9)	−0.0053 (8)	0.0062 (8)	0.0010 (8)
C5	0.0374 (11)	0.0499 (11)	0.0462 (11)	−0.0061 (8)	0.0045 (8)	−0.0007 (9)
O1	0.0385 (8)	0.0512 (8)	0.0806 (10)	−0.0040 (6)	−0.0037 (7)	−0.0002 (8)
C6	0.0466 (12)	0.0451 (11)	0.0511 (11)	−0.0032 (8)	0.0060 (9)	−0.0033 (9)
C7	0.0474 (12)	0.0442 (11)	0.0455 (11)	−0.0113 (8)	0.0072 (9)	−0.0056 (8)
C8	0.0390 (11)	0.0533 (12)	0.0517 (11)	−0.0077 (9)	−0.0016 (9)	−0.0039 (9)
C9	0.0418 (11)	0.0448 (11)	0.0485 (11)	−0.0020 (8)	0.0028 (8)	−0.0011 (8)
O2	0.0505 (9)	0.0485 (8)	0.0671 (9)	−0.0129 (6)	0.0012 (7)	−0.0081 (7)
C10	0.0521 (14)	0.0600 (13)	0.0706 (14)	−0.0201 (10)	0.0055 (11)	−0.0133 (11)
C11	0.0416 (11)	0.0451 (11)	0.0510 (11)	−0.0138 (9)	−0.0082 (9)	0.0026 (9)
C12	0.0386 (13)	0.0925 (17)	0.0606 (14)	−0.0154 (11)	0.0019 (10)	0.0154 (12)
C13	0.0488 (16)	0.177 (3)	0.0843 (19)	−0.0222 (18)	0.0083 (14)	0.044 (2)
C14	0.068 (2)	0.168 (3)	0.097 (2)	−0.049 (2)	−0.0050 (17)	0.068 (2)
C15	0.0709 (18)	0.0750 (17)	0.0855 (18)	−0.0386 (14)	−0.0308 (14)	0.0361 (14)

C16	0.0543 (13)	0.0409 (11)	0.0670 (13)	−0.0190 (10)	−0.0199 (11)	0.0028 (10)
C17	0.0742 (17)	0.0421 (12)	0.0733 (14)	0.0039 (11)	−0.0293 (12)	−0.0160 (11)
C18	0.105 (2)	0.0466 (14)	0.108 (2)	0.0161 (14)	−0.0562 (18)	−0.0294 (15)
C19	0.125 (3)	0.0394 (14)	0.124 (3)	−0.0210 (16)	−0.082 (2)	0.0112 (15)
C20	0.114 (3)	0.080 (2)	0.127 (3)	−0.056 (2)	−0.061 (2)	0.0490 (19)
C21	0.0492 (12)	0.0522 (12)	0.0403 (10)	−0.0096 (9)	−0.0050 (9)	0.0028 (9)
S1	0.0692 (4)	0.0499 (3)	0.0790 (4)	−0.0112 (3)	−0.0234 (3)	−0.0076 (3)
N3	0.0526 (11)	0.0499 (10)	0.0607 (10)	−0.0181 (8)	−0.0158 (8)	0.0122 (8)
C22	0.0467 (12)	0.0584 (13)	0.0360 (10)	−0.0129 (9)	−0.0055 (8)	0.0083 (9)
C23	0.0503 (12)	0.0588 (13)	0.0358 (10)	−0.0164 (10)	−0.0002 (8)	0.0081 (9)
C24	0.0514 (13)	0.0651 (13)	0.0459 (11)	−0.0063 (10)	0.0028 (9)	0.0078 (10)
C25	0.0412 (12)	0.0847 (17)	0.0532 (12)	−0.0121 (11)	0.0010 (9)	0.0001 (11)
C26	0.0512 (13)	0.0697 (15)	0.0507 (12)	−0.0208 (11)	−0.0028 (10)	−0.0012 (11)
C27	0.0540 (13)	0.0604 (13)	0.0466 (11)	−0.0157 (10)	−0.0042 (9)	0.0019 (10)
O3	0.0631 (10)	0.0515 (9)	0.0618 (9)	−0.0154 (7)	−0.0130 (7)	0.0138 (7)
C28	0.0714 (16)	0.0558 (14)	0.0570 (13)	−0.0106 (11)	0.0066 (11)	0.0007 (10)

Geometric parameters (Å, º)

N1—C21	1.365 (2)	C13—C14	1.343 (4)
N1—N2	1.399 (2)	C13—H13	0.9500
N1—N2	1.399 (2)	C14—C15	1.400 (4)
N1—C3	1.464 (2)	C14—H14	0.9500
N2—C1	1.295 (2)	C15—C20	1.414 (4)
C1—N2	1.295 (2)	C15—C16	1.430 (3)
C1—C4	1.448 (2)	C16—C17	1.410 (3)
C1—C2	1.499 (2)	C17—C18	1.377 (3)
C2—C3	1.536 (2)	C17—H17	0.9500
C2—H2A	0.9900	C18—C19	1.408 (5)
C2—H2B	0.9900	C18—H18	0.9500
C3—C11	1.515 (3)	C19—C20	1.332 (5)
C3—H3	1.0000	C19—H19	0.9500
C4—C9	1.400 (2)	C20—H20	0.9500
C4—C5	1.409 (2)	C21—N3	1.349 (2)
C5—O1	1.359 (2)	C21—S1	1.657 (2)
C5—C6	1.385 (2)	N3—C22	1.403 (2)
O1—H1	0.8400	N3—H3A	0.8800
C6—C7	1.380 (3)	C22—C27	1.391 (3)
C6—H6	0.9500	C22—C23	1.403 (3)
C7—O2	1.366 (2)	C23—C24	1.372 (3)
C7—C8	1.389 (3)	C23—O3	1.374 (2)
C8—C9	1.372 (2)	C24—C25	1.396 (3)
C8—H8	0.9500	C24—H24	0.9500
C9—H9	0.9500	C25—C26	1.361 (3)
O2—C10	1.424 (2)	C25—H25	0.9500
C10—H10A	0.9800	C26—C27	1.379 (3)
C10—H10B	0.9800	C26—H26	0.9500
C10—H10C	0.9800	C27—H27	0.9500

C11—C12	1.360 (3)	O3—C28	1.421 (2)
C11—C16	1.425 (3)	C28—H28A	0.9800
C12—C13	1.395 (3)	C28—H28B	0.9800
C12—H12	0.9500	C28—H28C	0.9800
C21—N1—N2	121.46 (15)	C14—C13—C12	120.0 (3)
C21—N1—N2	121.46 (15)	C14—C13—H13	120.0
C21—N1—C3	126.33 (15)	C12—C13—H13	120.0
N2—N1—C3	112.20 (13)	C13—C14—C15	121.8 (3)
N2—N1—C3	112.20 (13)	C13—C14—H14	119.1
C1—N2—N1	108.27 (14)	C15—C14—H14	119.1
N2—C1—C4	121.93 (16)	C14—C15—C20	123.5 (3)
N2—C1—C4	121.93 (16)	C14—C15—C16	118.7 (2)
N2—C1—C2	113.09 (15)	C20—C15—C16	117.8 (3)
N2—C1—C2	113.09 (15)	C17—C16—C11	123.1 (2)
C4—C1—C2	124.98 (15)	C17—C16—C15	118.7 (2)
C1—C2—C3	102.81 (14)	C11—C16—C15	118.1 (2)
C1—C2—H2A	111.2	C18—C17—C16	120.7 (3)
C3—C2—H2A	111.2	C18—C17—H17	119.7
C1—C2—H2B	111.2	C16—C17—H17	119.7
C3—C2—H2B	111.2	C17—C18—C19	119.9 (3)
H2A—C2—H2B	109.1	C17—C18—H18	120.0
N1—C3—C11	111.62 (16)	C19—C18—H18	120.0
N1—C3—C2	101.35 (14)	C20—C19—C18	120.4 (3)
C11—C3—C2	112.06 (14)	C20—C19—H19	119.8
N1—C3—H3	110.5	C18—C19—H19	119.8
C11—C3—H3	110.5	C19—C20—C15	122.4 (3)
C2—C3—H3	110.5	C19—C20—H20	118.8
C9—C4—C5	116.99 (16)	C15—C20—H20	118.8
C9—C4—C1	119.93 (16)	N3—C21—N1	112.16 (16)
C5—C4—C1	123.08 (16)	N3—C21—S1	126.88 (14)
O1—C5—C6	116.67 (17)	N1—C21—S1	120.95 (15)
O1—C5—C4	122.55 (16)	C21—N3—C22	132.25 (16)
C6—C5—C4	120.77 (17)	C21—N3—H3A	113.9
C5—O1—H1	109.5	C22—N3—H3A	113.9
C7—C6—C5	120.16 (18)	C27—C22—N3	127.24 (19)
C7—C6—H6	119.9	C27—C22—C23	119.08 (18)
C5—C6—H6	119.9	N3—C22—C23	113.67 (16)
O2—C7—C6	115.31 (17)	C24—C23—O3	125.16 (19)
O2—C7—C8	124.18 (17)	C24—C23—C22	120.62 (18)
C6—C7—C8	120.49 (17)	O3—C23—C22	114.21 (17)
C9—C8—C7	118.95 (18)	C23—C24—C25	119.3 (2)
C9—C8—H8	120.5	C23—C24—H24	120.4
C7—C8—H8	120.5	C25—C24—H24	120.4
C8—C9—C4	122.63 (18)	C26—C25—C24	120.3 (2)
C8—C9—H9	118.7	C26—C25—H25	119.8
C4—C9—H9	118.7	C24—C25—H25	119.8
C7—O2—C10	117.75 (16)	C25—C26—C27	121.11 (19)

O2—C10—H10A	109.5	C25—C26—H26	119.4
O2—C10—H10B	109.5	C27—C26—H26	119.4
H10A—C10—H10B	109.5	C26—C27—C22	119.6 (2)
O2—C10—H10C	109.5	C26—C27—H27	120.2
H10A—C10—H10C	109.5	C22—C27—H27	120.2
H10B—C10—H10C	109.5	C23—O3—C28	118.02 (16)
C12—C11—C16	120.0 (2)	O3—C28—H28A	109.5
C12—C11—C3	121.35 (18)	O3—C28—H28B	109.5
C16—C11—C3	118.59 (19)	H28A—C28—H28B	109.5
C11—C12—C13	121.3 (2)	O3—C28—H28C	109.5
C11—C12—H12	119.3	H28A—C28—H28C	109.5
C13—C12—H12	119.3	H28B—C28—H28C	109.5

C21—N1—N2—N2	0.00 (19)	C2—C3—C11—C16	−75.0 (2)
C3—N1—N2—N2	0.0 (2)	C16—C11—C12—C13	0.2 (3)
C21—N1—N2—C1	−170.99 (17)	C3—C11—C12—C13	−176.4 (2)
N2—N1—N2—C1	0 (100)	C11—C12—C13—C14	−1.5 (4)
C3—N1—N2—C1	9.8 (2)	C12—C13—C14—C15	1.1 (5)
N1—N2—C1—N2	0 (100)	C13—C14—C15—C20	−180.0 (3)
N2—N2—C1—C4	0.0 (9)	C13—C14—C15—C16	0.4 (4)
N1—N2—C1—C4	179.45 (15)	C12—C11—C16—C17	−177.63 (18)
N2—N2—C1—C2	0.0 (8)	C3—C11—C16—C17	−0.9 (3)
N1—N2—C1—C2	0.3 (2)	C12—C11—C16—C15	1.3 (3)
N2—C1—C2—C3	−9.4 (2)	C3—C11—C16—C15	177.99 (17)
N2—C1—C2—C3	−9.4 (2)	C14—C15—C16—C17	177.4 (2)
C4—C1—C2—C3	171.51 (16)	C20—C15—C16—C17	−2.3 (3)
C21—N1—C3—C11	−74.5 (2)	C14—C15—C16—C11	−1.6 (3)
N2—N1—C3—C11	104.57 (16)	C20—C15—C16—C11	178.78 (19)
N2—N1—C3—C11	104.57 (16)	C11—C16—C17—C18	−179.67 (18)
C21—N1—C3—C2	166.01 (18)	C15—C16—C17—C18	1.4 (3)
N2—N1—C3—C2	−14.88 (18)	C16—C17—C18—C19	−0.6 (3)
N2—N1—C3—C2	−14.88 (18)	C17—C18—C19—C20	0.8 (4)
C1—C2—C3—N1	13.60 (17)	C18—C19—C20—C15	−1.7 (4)
C1—C2—C3—C11	−105.54 (17)	C14—C15—C20—C19	−177.1 (3)
N2—C1—C4—C9	−175.47 (17)	C16—C15—C20—C19	2.5 (4)
N2—C1—C4—C9	−175.47 (17)	N2—N1—C21—N3	1.1 (3)
C2—C1—C4—C9	3.6 (3)	N2—N1—C21—N3	1.1 (3)
N2—C1—C4—C5	3.4 (3)	C3—N1—C21—N3	−179.84 (17)
N2—C1—C4—C5	3.4 (3)	N2—N1—C21—S1	−178.43 (13)
C2—C1—C4—C5	−177.52 (17)	N2—N1—C21—S1	−178.43 (13)
C9—C4—C5—O1	179.67 (17)	C3—N1—C21—S1	0.6 (3)
C1—C4—C5—O1	0.7 (3)	N1—C21—N3—C22	−167.46 (19)
C9—C4—C5—C6	0.2 (3)	S1—C21—N3—C22	12.1 (3)
C1—C4—C5—C6	−178.75 (17)	C21—N3—C22—C27	−9.8 (4)
O1—C5—C6—C7	−178.71 (18)	C21—N3—C22—C23	168.6 (2)
C4—C5—C6—C7	0.8 (3)	C27—C22—C23—C24	0.6 (3)
C5—C6—C7—O2	177.29 (16)	N3—C22—C23—C24	−177.93 (17)
C5—C6—C7—C8	−1.4 (3)	C27—C22—C23—O3	−179.93 (17)

O2—C7—C8—C9	−177.58 (17)	N3—C22—C23—O3	1.6 (2)
C6—C7—C8—C9	1.0 (3)	O3—C23—C24—C25	−179.18 (18)
C7—C8—C9—C4	0.0 (3)	C22—C23—C24—C25	0.3 (3)
C5—C4—C9—C8	−0.6 (3)	C23—C24—C25—C26	−0.3 (3)
C1—C4—C9—C8	178.38 (17)	C24—C25—C26—C27	−0.5 (3)
C6—C7—O2—C10	−178.99 (17)	C25—C26—C27—C22	1.3 (3)
C8—C7—O2—C10	−0.3 (3)	N3—C22—C27—C26	176.93 (18)
N1—C3—C11—C12	−11.2 (2)	C23—C22—C27—C26	−1.4 (3)
C2—C3—C11—C12	101.7 (2)	C24—C23—O3—C28	5.4 (3)
N1—C3—C11—C16	172.14 (15)	C22—C23—O3—C28	−174.03 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.84	1.96	2.6889 (19)	145
C18—H18···S1^{i}	0.95	2.96	3.712 (2)	137

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