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The crystal structure of 1,5-dibenzyl-1*H*-pyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione

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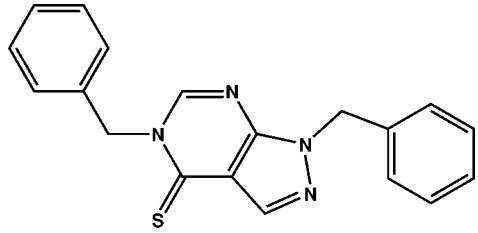
In the title compound, $C_{19}H_{16}N_4S$, the pyrazolo[3,4-*d*]pyrimidine ring is close to being planar, with the greatest deviation from the mean plane being 0.023 (2) Å for the C atom bearing the thione S atom. The two phenyl rings are nearly perpendicular to the fused ring system [dihedral angles = 71.4 (2) and 78.1 (2)°], but are oriented in opposite directions; the dihedral angle between the phenyl rings is 32.22 (16)°. In the crystal, linear supramolecular chains along [101] are sustained by C—H···S interactions.

Keywords: crystal structure; pyrazolo[3,4-*d*]pyrimidine; thione; C—H···S interactions.

CCDC reference: 1041681

1. Related literature

For pharmacological and biochemical properties of pyrazolo[1,5-*a*]pyrimidine, see: Orlikova *et al.* (2014); Yuan *et al.* (2013); Rashad *et al.* (2011). For related structures, see: El Fal *et al.* (2013, 2014); Alsubari *et al.* (2011); Ramli *et al.* (2012).



2. Experimental

2.1. Crystal data

$C_{19}H_{16}N_4S$
M_r = 332.42
Monoclinic, $P2_1$
a = 4.4953 (12) Å
b = 29.140 (8) Å
c = 6.3889 (16) Å
β = 97.860 (9)°
V = 829.0 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 296 K
0.37 × 0.34 × 0.29 mm

2.2. Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.589, T_{max} = 0.746
9214 measured reflections
3582 independent reflections
2406 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.084
S = 0.97
3582 reflections
217 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Absolute structure: Flack & Bernardinelli (2000), 1730 Friedel pairs
Absolute structure parameter: −0.11 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···S1^{i}	0.93	2.87	3.784 (3)	167

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT-Plus* (Bruker, 2009); 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: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Acknowledgements

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray measurements and the University Mohammed V, Rabat, Morocco, for financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5354).

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supporting information

Acta Cryst. (2015). E**71**, o95–o96 [doi:10.1107/S205698901402828X]

The crystal structure of 1,5-dibenzyl-1*H*-pyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione

Mohammed El Fal, Youssef Ramli, El Mokhtar Essassi, Mohamed Saadi and Lahcen El Ammari

S1. Structural commentary

Pyrazolo[3,4-d] pyrimidine-4-thione are intermediate sub-units useful for the development of molecules of pharmaceutical interest. They have found applications in various therapeutic areas, including anti-inflammatory, anti-tumour and anti-cancer (Orlikova *et al.*, 2014; Yuan *et al.*, 2013; Rashad *et al.*, 2011). The present paper is a continuation of our research work devoted to the development of pyrazolo[3,4-*d*] pyrimidine derivatives with potential pharmacological activities (El Fal *et al.*, 2013; El Fal *et al.*, 2014; Alsubari *et al.*, 2011; Ramli *et al.*, 2012).

The molecule of the title compound is build up from two fused five- and six-membered heterocycles linked to two phenyl rings *via* two –CH_2– groups as shown in Fig. 1. The pyrazolo[3,4-*d*]pyrimidine system is virtually planar with the largest deviation from the mean plane being -0.023 (2) Å at C1 and makes dihedral angles of 71.4 (2)° and 78.1 (2)° with the mean plane through the first (C7 to C12) and the second (C14 to C19) phenyl rings, respectively. As a matter of fact, the two phenyl rings are oriented in opposite direction to the plane of the fused rings. No classic hydrogen bonds are observed in the present structure.

S2. Synthesis and crystallization

3.32 g (10 mmol) of 1,5-dibenzyl-1H, 4H, 5*H*-pyrazolo [3,4-d] pyrimidin-4-one is refluxed in pyridine (30 ml) with 5.55 g (25 mmol) of phosphorus pentasulfide for 4 h. Then the solvent was evaporated under reduced pressure. The precipitate that formed was washed with hot water to remove residual dimerized P_2S_5 until colourless filtrate was noted. The solid was re-crystallized from ethanol to afford the title compound as yellow crystals (yield: 85%; m.p. = 563 K).

S3. Refinement

The H atoms were located in a difference map and treated as riding with C—H = 0.93 Å (aromatic) and C—H = 0.97 Å (methylene). All hydrogen with U_{iso}(H) = 1.2 U_{eq} (aromatic and methylene). Two reflections, *i.e.* 0 -2 0 and 0 2 0, were omitted fro the final refinement owing to poor agreement.

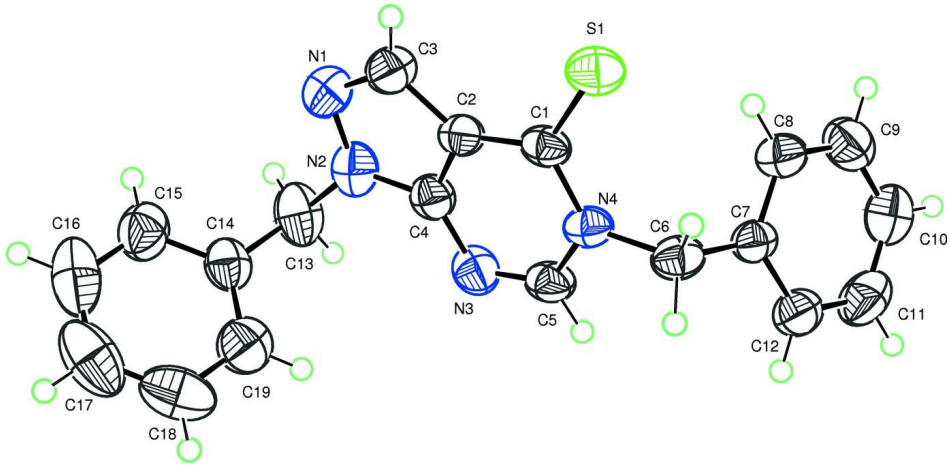

Figure 1

Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

1,5-Dibenzyl-1*H*-pyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione

Crystal data

$C_{19}H_{16}N_4S$
$M_r = 332.42$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 4.4953$ (12) Å
$b = 29.140$ (8) Å
$c = 6.3889$ (16) Å
$\beta = 97.860$ (9)°
$V = 829.0$ (4) Å^3
$Z = 2$
$F(000) = 348$
$D_x = 1.332$ Mg m^{-3}
Melting point: 563 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3582 reflections
$\theta = 2.8$–27.1°
$\mu = 0.20$ mm^{-1}
$T = 296$ K
Block, yellow
0.37 × 0.34 × 0.29 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.589$, $T_{max} = 0.746$
9214 measured reflections
3582 independent reflections
2406 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 27.1°$, $\theta_{min} = 2.8°$
$h = -5\rightarrow5$
$k = -37\rightarrow37$
$l = -8\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.084$
$S = 0.97$
3582 reflections
217 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}

Absolute structure: Flack & Bernardinelli (2000), 1730 Friedel pairs

Absolute structure parameter: −0.11 (7)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5941 (5)	0.48633 (8)	0.9980 (3)	0.0412 (6)
C2	0.4720 (5)	0.44502 (8)	1.0570 (3)	0.0411 (6)
C3	0.5145 (7)	0.41623 (9)	1.2377 (4)	0.0586 (7)
H3	0.6506	0.4222	1.3578	0.070*
C4	0.2489 (6)	0.42310 (9)	0.9208 (4)	0.0457 (6)
C5	0.2551 (6)	0.47501 (9)	0.6716 (4)	0.0488 (6)
H5	0.1885	0.4864	0.5375	0.059*
C6	0.5892 (5)	0.54088 (9)	0.6906 (4)	0.0477 (6)
H6A	0.6197	0.5330	0.5476	0.057*
H6B	0.7826	0.5495	0.7672	0.057*
C7	0.3812 (5)	0.58142 (8)	0.6832 (4)	0.0425 (6)
C8	0.3274 (6)	0.60388 (9)	0.8650 (4)	0.0545 (7)
H8	0.4188	0.5935	0.9959	0.065*
C9	0.1404 (7)	0.64137 (10)	0.8546 (5)	0.0651 (8)
H9	0.1070	0.6563	0.9780	0.078*
C10	0.0034 (7)	0.65686 (11)	0.6635 (5)	0.0700 (8)
H10	−0.1242	0.6821	0.6569	0.084*
C11	0.0546 (7)	0.63514 (11)	0.4817 (5)	0.0701 (9)
H11	−0.0375	0.6458	0.3515	0.084*
C12	0.2421 (6)	0.59761 (9)	0.4912 (4)	0.0551 (7)
H12	0.2754	0.5830	0.3671	0.066*
C13	−0.0331 (7)	0.34855 (9)	0.9311 (5)	0.0701 (9)
H13A	−0.1746	0.3609	0.8167	0.084*
H13B	−0.1461	0.3374	1.0396	0.084*
C14	0.1353 (6)	0.30957 (9)	0.8500 (5)	0.0538 (7)
C15	0.1948 (7)	0.27009 (11)	0.9677 (5)	0.0701 (8)
H15	0.1235	0.2673	1.0970	0.084*
C16	0.3567 (8)	0.23521 (11)	0.8969 (8)	0.0926 (12)
H16	0.3946	0.2088	0.9778	0.111*
C17	0.4635 (8)	0.23889 (15)	0.7078 (9)	0.0961 (13)
H17	0.5758	0.2152	0.6605	0.115*
C18	0.4049 (8)	0.27764 (16)	0.5874 (6)	0.0898 (11)
H18	0.4766	0.2801	0.4581	0.108*

C19	0.2406 (7)	0.31279 (11)	0.6575 (5)	0.0705 (8)
H19	0.2000	0.3389	0.5748	0.085*
N1	0.3381 (6)	0.38019 (8)	1.2147 (4)	0.0633 (6)
N2	0.1709 (5)	0.38498 (7)	1.0188 (4)	0.0575 (6)
N3	0.1303 (5)	0.43742 (7)	0.7249 (3)	0.0529 (5)
N4	0.4758 (4)	0.49978 (6)	0.7928 (3)	0.0422 (5)
S1	0.85051 (15)	0.51743 (3)	1.14918 (10)	0.0571 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0382 (13)	0.0485 (15)	0.0369 (13)	0.0091 (11)	0.0049 (10)	−0.0077 (11)
C2	0.0406 (14)	0.0454 (15)	0.0366 (13)	0.0074 (11)	0.0030 (11)	−0.0022 (11)
C3	0.0693 (19)	0.0591 (18)	0.0468 (16)	0.0095 (16)	0.0061 (14)	0.0028 (14)
C4	0.0446 (15)	0.0458 (16)	0.0474 (15)	0.0080 (12)	0.0087 (13)	−0.0024 (13)
C5	0.0507 (16)	0.0561 (18)	0.0367 (13)	0.0104 (14)	−0.0046 (11)	−0.0056 (12)
C6	0.0459 (15)	0.0593 (16)	0.0395 (14)	−0.0032 (13)	0.0116 (12)	0.0003 (12)
C7	0.0424 (15)	0.0473 (14)	0.0375 (14)	−0.0095 (12)	0.0049 (11)	0.0009 (12)
C8	0.0618 (18)	0.0591 (18)	0.0412 (15)	−0.0018 (14)	0.0023 (13)	0.0010 (13)
C9	0.071 (2)	0.0571 (19)	0.069 (2)	−0.0002 (16)	0.0151 (17)	−0.0094 (15)
C10	0.071 (2)	0.0573 (19)	0.082 (2)	0.0038 (16)	0.0097 (17)	0.0114 (18)
C11	0.073 (2)	0.073 (2)	0.0607 (19)	0.0017 (18)	−0.0028 (16)	0.0207 (17)
C12	0.0593 (18)	0.0584 (18)	0.0467 (15)	−0.0083 (15)	0.0040 (13)	0.0037 (13)
C13	0.0531 (18)	0.0551 (19)	0.102 (2)	−0.0104 (15)	0.0102 (17)	−0.0024 (16)
C14	0.0479 (16)	0.0475 (16)	0.0647 (18)	−0.0101 (12)	0.0028 (14)	−0.0036 (14)
C15	0.074 (2)	0.0588 (19)	0.076 (2)	−0.0095 (17)	0.0032 (16)	0.0059 (17)
C16	0.079 (3)	0.053 (2)	0.140 (4)	0.0019 (19)	−0.006 (3)	0.003 (2)
C17	0.062 (2)	0.080 (3)	0.144 (4)	0.000 (2)	0.004 (3)	−0.041 (3)
C18	0.076 (3)	0.116 (3)	0.077 (2)	−0.014 (2)	0.0093 (19)	−0.036 (3)
C19	0.069 (2)	0.069 (2)	0.072 (2)	−0.0072 (16)	0.0068 (17)	−0.0002 (16)
N1	0.0782 (18)	0.0568 (16)	0.0564 (15)	−0.0011 (13)	0.0142 (13)	0.0070 (12)
N2	0.0550 (15)	0.0504 (14)	0.0681 (16)	0.0002 (11)	0.0118 (12)	0.0033 (13)
N3	0.0503 (13)	0.0496 (14)	0.0558 (14)	0.0029 (11)	−0.0034 (11)	−0.0043 (11)
N4	0.0406 (11)	0.0509 (12)	0.0342 (10)	0.0034 (9)	0.0021 (9)	−0.0013 (9)
S1	0.0536 (4)	0.0676 (4)	0.0463 (4)	−0.0042 (4)	−0.0073 (3)	−0.0052 (4)

Geometric parameters (Å, º)

C1—C2	1.396 (3)	C10—C11	1.370 (4)
C1—N4	1.402 (3)	C10—H10	0.9300
C1—S1	1.667 (2)	C11—C12	1.377 (4)
C2—C4	1.390 (3)	C11—H11	0.9300
C2—C3	1.419 (3)	C12—H12	0.9300
C3—N1	1.312 (3)	C13—N2	1.463 (3)
C3—H3	0.9300	C13—C14	1.496 (4)
C4—N2	1.345 (3)	C13—H13A	0.9700
C4—N3	1.357 (3)	C13—H13B	0.9700
C5—N3	1.297 (3)	C14—C19	1.380 (4)

C5—N4	1.376 (3)	C14—C15	1.380 (4)
C5—H5	0.9300	C15—C16	1.363 (5)
C6—N4	1.487 (3)	C15—H15	0.9300
C6—C7	1.503 (3)	C16—C17	1.364 (5)
C6—H6A	0.9700	C16—H16	0.9300
C6—H6B	0.9700	C17—C18	1.371 (5)
C7—C12	1.381 (3)	C17—H17	0.9300
C7—C8	1.383 (3)	C18—C19	1.373 (5)
C8—C9	1.374 (4)	C18—H18	0.9300
C8—H8	0.9300	C19—H19	0.9300
C9—C10	1.367 (4)	N1—N2	1.376 (3)
C9—H9	0.9300		

C2—C1—N4	112.4 (2)	C11—C12—C7	120.7 (3)
C2—C1—S1	125.35 (18)	C11—C12—H12	119.6
N4—C1—S1	122.28 (18)	C7—C12—H12	119.6
C4—C2—C1	120.3 (2)	N2—C13—C14	111.3 (2)
C4—C2—C3	104.1 (2)	N2—C13—H13A	109.4
C1—C2—C3	135.7 (2)	C14—C13—H13A	109.4
N1—C3—C2	111.7 (3)	N2—C13—H13B	109.4
N1—C3—H3	124.1	C14—C13—H13B	109.4
C2—C3—H3	124.1	H13A—C13—H13B	108.0
N2—C4—N3	126.1 (2)	C19—C14—C15	118.5 (3)
N2—C4—C2	107.4 (2)	C19—C14—C13	120.5 (3)
N3—C4—C2	126.5 (2)	C15—C14—C13	120.9 (3)
N3—C5—N4	126.9 (2)	C16—C15—C14	120.9 (3)
N3—C5—H5	116.6	C16—C15—H15	119.6
N4—C5—H5	116.6	C14—C15—H15	119.6
N4—C6—C7	113.42 (17)	C15—C16—C17	120.3 (4)
N4—C6—H6A	108.9	C15—C16—H16	119.9
C7—C6—H6A	108.9	C17—C16—H16	119.9
N4—C6—H6B	108.9	C16—C17—C18	119.8 (4)
C7—C6—H6B	108.9	C16—C17—H17	120.1
H6A—C6—H6B	107.7	C18—C17—H17	120.1
C12—C7—C8	118.3 (2)	C17—C18—C19	120.1 (4)
C12—C7—C6	120.0 (2)	C17—C18—H18	119.9
C8—C7—C6	121.7 (2)	C19—C18—H18	119.9
C9—C8—C7	120.7 (3)	C18—C19—C14	120.3 (3)
C9—C8—H8	119.6	C18—C19—H19	119.8
C7—C8—H8	119.6	C14—C19—H19	119.8
C10—C9—C8	120.3 (3)	C3—N1—N2	105.5 (2)
C10—C9—H9	119.9	C4—N2—N1	111.2 (2)
C8—C9—H9	119.9	C4—N2—C13	127.6 (2)
C9—C10—C11	119.8 (3)	N1—N2—C13	120.7 (2)
C9—C10—H10	120.1	C5—N3—C4	111.8 (2)
C11—C10—H10	120.1	C5—N4—C1	122.1 (2)
C10—C11—C12	120.1 (3)	C5—N4—C6	116.1 (2)
C10—C11—H11	119.9	C1—N4—C6	121.78 (19)

C12—C11—H11	119.9

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···S1^{i}	0.93	2.87	3.784 (3)	167

Symmetry code: (i) *x*−1, *y*, *z*−1.