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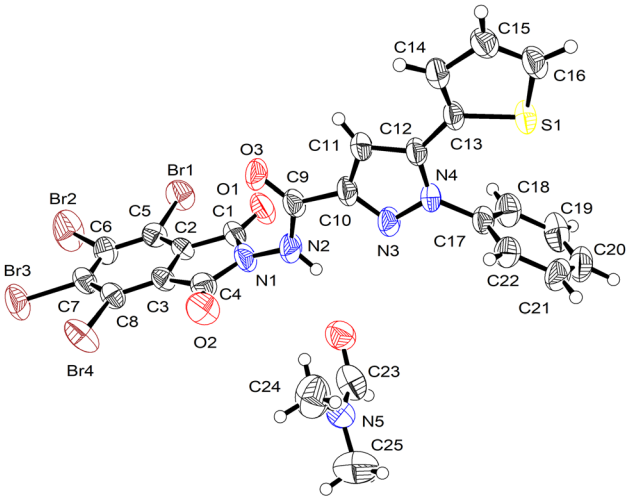
The crystal structure of 1-phenyl-*N*-(4,5,6,7-tetrabromo-1,3-dioxoisoindolin-2-yl)-5-(thiophen-2-yl)-1*H*-pyrazole-3-carboxamide-dimethylformamide (1/1) $C_{22}H_{10}Br_4N_4O_3S$



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Abstract

$C_{22}H_{10}Br_4N_4O_3S$, monoclinic, $P2_1/c$ (no. 14), a = 9.3725(6) Å, b = 20.0436(12) Å, c = 15.3281(11) Å, β = 102.896(6)°, V = 2806.9(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0575, $wR_{ref}(F^2)$ = 0.1566, T = 296 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.41 × 0.32 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.85 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	29.8°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23925, 6975, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4306
$N(param)_{refined}$:	354
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

A mixture of 1-phenyl-5-(thiophen-2-yl)-1*H*-pyrazole-3-carbohydrazide (0.57 g, 2.0 mmol) and 4,5,6,7-tetrabromoisobenzofuran-1,3-dione (0.93 g, 2.0 mmol) in glacial acetic acid (10 mL) was refluxed for 6 h. The solid obtained on cooling was collected by filtration, washed with cold water, dried, and recrystallized from dimethylformamide to give colourless crystals (82%) of the title compound.

Experimental details

Hydrogen atoms were identified in difference Fourier syntheses. The methyl hydrogens and those bonded to sp^2 C and N atoms were idealized during refinement using options AFIX 137, and AFIX 43 respectively in the SHELXL-2018 program [4]. The U_{iso} values of the hydrogen atoms were set to 1.5U_{eq}(C) for methyl groups and 1.2U_{eq}(C,N) for the rest.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	X	Y	z	U_{iso}*/U_{eq}
C1	0.3083 (5)	0.6298 (2)	0.1206 (4)	0.0475 (12)
C2	0.1607 (5)	0.6155 (2)	0.0648 (3)	0.0412 (11)
C3	0.0852 (5)	0.5758 (2)	0.1148 (3)	0.0417 (11)
C4	0.1825 (6)	0.5627 (2)	0.2043 (4)	0.0493 (12)
C5	0.0951 (6)	0.6389 (2)	−0.0187 (3)	0.0460 (11)
C6	−0.0518 (6)	0.6221 (3)	−0.0527 (3)	0.0508 (13)
C7	−0.1275 (6)	0.5820 (2)	−0.0044 (3)	0.0498 (12)
C8	−0.0602 (5)	0.5586 (2)	0.0801 (3)	0.0452 (11)
C9	0.4315 (5)	0.6582 (2)	0.3253 (3)	0.0469 (12)
C10	0.5649 (5)	0.6670 (2)	0.3971 (3)	0.0452 (12)
C11	0.5900 (5)	0.7179 (2)	0.4606 (3)	0.0456 (12)
H11	0.527087	0.752500	0.466898	0.055*
C12	0.7281 (5)	0.7059 (2)	0.5120 (3)	0.0433 (11)
C13	0.8070 (5)	0.7430 (2)	0.5895 (3)	0.0417 (11)
C14	0.7455 (5)	0.7895 (2)	0.6354 (3)	0.0484 (12)
H14	0.647451	0.801787	0.619772	0.058*
C15	0.8472 (6)	0.8167 (3)	0.7090 (4)	0.0520 (13)
H15	0.822546	0.848074	0.747882	0.062*
C16	0.9835 (6)	0.7925 (3)	0.7167 (3)	0.0529 (13)
H16	1.063670	0.805795	0.760762	0.063*
C17	0.9180 (5)	0.6184 (2)	0.5026 (3)	0.0432 (11)
C18	1.0233 (6)	0.6309 (3)	0.4555 (4)	0.0582 (14)
H18	1.005284	0.660775	0.407920	0.070*
C19	1.1569 (7)	0.5985 (4)	0.4796 (4)	0.0735 (18)
H19	1.229310	0.606346	0.448054	0.088*
C20	1.1818 (7)	0.5548 (3)	0.5500 (5)	0.0714 (19)
H20	1.271037	0.532637	0.565475	0.086*
C21	1.0780 (7)	0.5434 (3)	0.5977 (4)	0.0608 (16)
H21	1.097368	0.514172	0.646115	0.073*
C22	0.9439 (6)	0.5750 (3)	0.5745 (3)	0.0500 (12)
H22	0.872297	0.567319	0.606672	0.060*
C23	0.5915 (8)	0.4229 (4)	0.2523 (5)	0.0768 (19)
H23	0.653677	0.402742	0.220602	0.092*
C24	0.4352 (9)	0.4134 (4)	0.3554 (6)	0.099 (2)
H24A	0.422922	0.460305	0.343737	0.148*
H24B	0.477006	0.406383	0.417820	0.148*
H24C	0.341717	0.391603	0.339489	0.148*
C25	0.5621 (12)	0.3167 (4)	0.3171 (8)	0.133 (4)
H25A	0.617900	0.300313	0.276181	0.199*
H25B	0.471164	0.292791	0.308253	0.199*
H25C	0.616523	0.310192	0.377445	0.199*
N1	0.3136 (4)	0.5956 (2)	0.2005 (3)	0.0508 (11)
N2	0.4285 (5)	0.6030 (2)	0.2736 (3)	0.0590 (12)
H2	0.496421	0.573406	0.286166	0.071*
N3	0.6792 (4)	0.6258 (2)	0.4052 (3)	0.0487 (10)
N4	0.7777 (4)	0.65039 (19)	0.4759 (3)	0.0446 (10)
N5	0.5336 (5)	0.3853 (2)	0.3017 (4)	0.0611 (12)
O1	0.4055 (4)	0.6630 (2)	0.1052 (3)	0.0688 (11)
O2	0.1604 (5)	0.5332 (2)	0.2673 (3)	0.0661 (11)
O3	0.3303 (4)	0.69731 (18)	0.3140 (2)	0.0584 (10)
O4	0.5723 (5)	0.4854 (2)	0.2424 (3)	0.0674 (11)
Br1	0.19755 (7)	0.69503 (3)	−0.08170 (4)	0.0665 (2)
Br2	−0.14640 (9)	0.65636 (5)	−0.16509 (5)	0.0999 (3)
Br3	−0.32399 (7)	0.55998 (4)	−0.05413 (5)	0.0788 (2)
Br4	−0.16683 (8)	0.50983 (3)	0.14779 (4)	0.0719 (2)
S1	0.99228 (14)	0.73488 (7)	0.63679 (9)	0.0529 (3)

Comment

Carbohydrazides containing the pyrazole ring system have significant biological activities [5, 6]. Heterocycles containing both pyrazoles and thiophene ring systems are versatile intermediates in organic synthesis and have many medicinal applications [7–9]. Recently, the X-ray crystal structures of related heterocycles containing the pyrazole ring system have been reported by us [10–12].

The asymmetric unit of the crystal structure consists of one molecule of the title compound and one molecule of dimethylformamide solvent. The target molecule comprises tetrabromodioxoisoindolinyl (A [C1—C8, O1, O2, Br1—Br4]), pyrazolyl (B [C10—C12, N3, N4]), thiophenyl (C [C13—C16, S1]) and phenyl (D [C17—C22]) ring systems. In the title molecule, fragments B, C and the carboxamide group are almost co-planar with twist angles: carboxamide/B = 3.9(8)° and B/C = 13.9(3)°. Ring systems A and D are almost perpendicular to the B–C-carboxamide plane with twist angles A/B = 90.56(12)° and B/D = 79.97(16)°.

In the crystal, an intermolecular N–H···O hydrogen bond occurs between the target and solvent molecules. The associated geometry is N2···O4 = 2.808(6) Å, N2–H2···O4 = 143.7°.

Close C–H···O interactions with geometry: (C14···O1 = 3.259(6) Å, C14–H14···O1 = 170.7°) and (C16···O3 = 3.266(6) Å, C16–H16···O3 = 146.4°) link molecules in the [100] direction. Two phenyl groups (D) of neighbouring molecules, related by inversion symmetry, are involved in a π-π contact with a centroid-centroid distance of 3.65 Å.

The tetrabromodioxoisoindolinyl group (A) of one molecule is also involved in π-π contacts on both sides. On one side is a crystallographically independent group of a molecule related by inversion symmetry (A–A interplanar distance = 3.67 Å) and on the other side is a thiophenyl group (A-[C2,C3,C5,C6,C7,C8 ring] centroid-to-centroid distance = 3.61 Å).

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