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7-(4-Fluorobenzylidene)-3-(4-fluorophenyl)-*N*-phenyl-3,3*a*,4,5,6,7-hexahydro-2*H*-indazole-2-carbothioamide–dimethylformamide (2/1), $C_{27}H_{23}F_2N_3S$, 0.5(C_3H_7NO)

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Abstract

$C_{27}H_{23}F_2N_3S$, 0.5(C_3H_7NO), monoclinic, $C2/c$ (no. 15), $a = 25.1579(10)$ Å, $b = 9.9356(4)$ Å, $c = 20.1799(7)$ Å, $\beta = 91.741(4)^\circ$, $V = 5041.8(3)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0508$, $wR_{ref}(F^2) = 0.1385$, $T = 296(2)$ 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 needle
Size:	$0.52 \times 0.31 \times 0.11$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.17 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	29.9° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23341, 6338, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4290
$N(\text{param})_{\text{refined}}$:	345
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The title compound was synthesized from reaction of equimolar quantities of 7-(4-fluorobenzylidene)-3-(4-fluorophenyl)-3,3*a*,4,5,6,7-hexahydro-2*H*-indazole and phenyl isothiocyanate in anhydrous ethanol under reflux for 2 h. The crude product was collected by filtration, washed with ethanol and recrystallized from dimethylformamide to give the title compound in 82% yield as colourless crystals (Mp. 228–230 °C).

Experimental details

All hydrogen atoms were placed in calculated positions and refined using a riding model. The N–H bond was fixed at 0.86 Å (AFIX 43 instruction in SHELXL [2, 3]), with displacement parameters set to 1.2 times $U_{eq}(N)$. C–H distances for sp^2 carbon atoms were set to 0.93 Å (AFIX 43) and $U_{iso}(H)$ set to 1.2 times $U_{eq}(C)$. The methine C–H distance was set to 0.98 Å (AFIX 13) and $U_{iso}(H)$ set to 1.2 times $U_{eq}(C)$. The methylene C–H distances were set to 0.97 Å (AFIX 23) and $U_{iso}(H)$ set to 1.2 times $U_{eq}(C)$. Methyl C–H distances were set to 0.96 Å and $U_{iso}(H)$ set to 1.5 times $U_{eq}(C)$ with the group allowed to rotate about the C–C bond (AFIX 137).

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.92723(8)	0.1198(3)	0.69906(10)	0.0697(6)
C2	0.93112(8)	0.2553(3)	0.70272(12)	0.0826(7)
H2	0.96304(3)	0.29822(4)	0.69421(2)	0.099*
C3	0.88650(8)	0.3296(2)	0.71946(11)	0.0707(6)
H3	0.88856(2)	0.42300(1)	0.72137(3)	0.085*
C4	0.83934(7)	0.26626(18)	0.73320(8)	0.0496(4)
C5	0.83759(7)	0.1282(2)	0.72919(11)	0.0642(5)
H5	0.80614(0)	0.08381(4)	0.73846(9)	0.077*
C6	0.88153(8)	0.0535(2)	0.71168(11)	0.0729(6)
H6	0.87971(3)	−0.03976(3)	0.70866(1)	0.087*
C7	0.79256(7)	0.34778(18)	0.75499(8)	0.0488(4)
H7	0.79801(3)	0.44265(1)	0.74376(9)	0.059*
C8	0.78232(7)	0.33495(17)	0.82986(8)	0.0482(4)
H8	0.80271(0)	0.25826(7)	0.84759(6)	0.058*
C9	0.72445(7)	0.30129(16)	0.83089(8)	0.0451(4)
C10	0.69490(7)	0.30085(17)	0.89248(8)	0.0482(4)
C11	0.71386(8)	0.40701(19)	0.94150(9)	0.0594(5)
H11A	0.70380(3)	0.38020(8)	0.98560(7)	0.071*
H11B	0.69591(9)	0.49111(2)	0.93102(4)	0.071*
C12	0.77351(8)	0.4304(2)	0.94189(9)	0.0672(5)
H12A	0.79140(0)	0.35192(6)	0.96047(4)	0.081*
H12B	0.78213(7)	0.50655(9)	0.97030(9)	0.081*
C13	0.79426(8)	0.4573(2)	0.87305(9)	0.0618(5)
H13A	0.77707(7)	0.53631(5)	0.85401(6)	0.074*
H13B	0.83228(9)	0.47346(3)	0.87577(5)	0.074*
C14	0.72320(7)	0.33496(17)	0.66250(8)	0.0486(4)
C15	0.63994(7)	0.32426(17)	0.59232(8)	0.0477(4)
C16	0.65760(7)	0.29135(18)	0.53006(8)	0.0538(4)
H16	0.69241(6)	0.26268(3)	0.52487(6)	0.065*
C17	0.62300(8)	0.30144(19)	0.47552(9)	0.0599(5)
H17	0.63490(9)	0.28032(4)	0.43359(6)	0.072*
C18	0.57145(9)	0.3422(2)	0.48264(10)	0.0663(5)
H18	0.54850(4)	0.34768(8)	0.44573(3)	0.080*
C19	0.55367(8)	0.3748(2)	0.54429(11)	0.0674(5)
H19	0.51859(8)	0.40162(5)	0.54926(5)	0.081*
C20	0.58811(7)	0.3677(2)	0.59897(9)	0.0579(4)
H20	0.57632(9)	0.39225(7)	0.64050(0)	0.070*
C21	0.65562(7)	0.21164(18)	0.89975(8)	0.0514(4)
H21	0.64972(6)	0.15414(9)	0.86391(2)	0.062*
C22	0.62046(7)	0.19049(18)	0.95540(9)	0.0530(4)
C23	0.60158(7)	0.0611(2)	0.96603(10)	0.0612(5)
H23	0.60998(4)	−0.00679(3)	0.93641(9)	0.073*
C24	0.57063(8)	0.0307(2)	1.01942(11)	0.0741(6)
H24	0.55849(4)	−0.05644(0)	1.02634(9)	0.089*
C25	0.55852(9)	0.1322(3)	1.06145(12)	0.0772(6)
C26	0.57458(9)	0.2611(2)	1.05289(12)	0.0783(6)
H26	0.56494(0)	0.32817(0)	1.08236(7)	0.094*
C27	0.60562(8)	0.2909(2)	0.99935(11)	0.0667(5)
H27	0.61670(5)	0.37903(6)	0.99262(0)	0.080*
N1	0.74100(5)	0.30100(14)	0.72527(6)	0.0477(3)
N2	0.70220(5)	0.28201(14)	0.77347(6)	0.0477(3)
N3	0.67126(6)	0.30801(16)	0.65128(7)	0.0529(4)
H3A	0.65477(9)	0.27648(6)	0.68461(4)	0.063*
S1	0.76395(2)	0.40457(7)	0.60911(2)	0.0751(2)
F1	0.97061(5)	0.04890(18)	0.68091(7)	0.1032(5)
F2	0.52817(7)	0.10352(17)	1.11445(9)	0.1232(6)
C28 ^a	0.5459(3)	0.1446(7)	0.7054(3)	0.1081(19)
H28 ^a	0.53516(6)	0.13065(9)	0.66141(7)	0.130*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C29 ^a	0.5241(3)	0.1818(9)	0.8189(3)	0.120(2)
H29A ^a	0.52578(0)	0.27531(5)	0.83062(2)	0.180*
H29B ^a	0.55875(4)	0.14226(7)	0.82441(3)	0.180*
H29C ^a	0.49972(1)	0.13637(4)	0.84697(9)	0.180*
C30 ^a	0.4526(3)	0.1886(10)	0.7310(5)	0.154(4)
H30A ^a	0.45116(0)	0.21038(2)	0.68460(7)	0.230*
H30B ^a	0.43753(5)	0.26095(4)	0.75569(2)	0.230*
H30C ^a	0.43280(8)	0.10759(0)	0.73823(2)	0.230*
N4 ^a	0.5064(7)	0.1690(4)	0.7523(8)	0.091(2)
O1 ^a	0.59251(18)	0.1408(6)	0.7192(3)	0.1327(18)

^aOccupancy: 0.5.

The dimethylformamide molecule lies on a two-fold rotation axis and was refined with restrained geometry and displacement parameters (DFIX, SIMU).

Comment

Pyrazole containing compounds are an essential core scaffold in many natural products and show various biological activities [5–7]. Several synthetic pathways have been reported for the synthesis of pyrazoles [8–10].

The asymmetric unit consists of one molecule of the title compound and half a molecule of dimethyl formamide solvent located on a two-fold rotation axis (see the figure). Geometric parameters are all in the expected ranges [11]. The molecule consists of two fluorophenyl groups [**A** (F1, C1–C6) and **D** (F2, C22–C26)], a hexahydroindazolyl group [**B** (N1, N2, C7–C13)] and a phenyl group [**C** (C15–C20)]. The cyclohexane segment (C8–C13) of **B** is in chair conformation. The pyrazolyl ring of **B** assumes an envelop conformation although it is nearly planar with the flap (C7) deviating by only 0.132(3) Å from the plane of the rest of the ring (C8, C9, N1, N2). An intramolecular contact is observed (N3–H3A···N2) and the same hydrogen atom also interacts with the DMF solvent molecule (N3–H3A···O1). C–H···F and C–H···S interactions form an extended network in the crystal structure. Edge-to-face interaction occurs between the phenyl (**C**) and fluorophenyl (**D**) rings with a centroid-to-centroid distance of 5.1 Å.

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