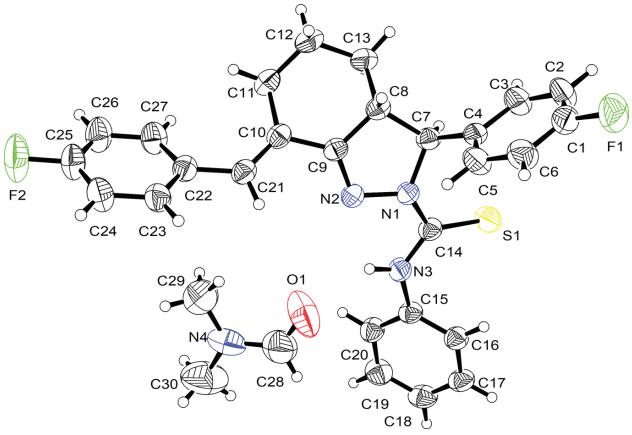
Obaid Fahad Aldosari, Bakr F. Abdel-Wahab, Mohammad Hayal Alotaibi, Amany S. Hegazy, Benson M. Kariuki* and Gamal A. El-Hiti*

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)



https://doi.org/10.1515/ncrs-2019-0261
Received April 9, 2019; accepted June 5, 2019; available online August 17, 2019

Abstract

$C_{27}H_{23}F_2N_3S$, 0.5(C_3H_7NO), monoclinic, *C*2/*c* (no. 15), $a = 25.1579(10)$ Å, $b = 9.9356(4)$ Å, $c = 20.1799(7)$ Å, $\beta = 91.741(4)°$, $V = 5041.8(3)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0508$, $wR_{ref}(F^2) = 0.1385$, $T = 296(2)$ K.

***Corresponding authors: Benson M. Kariuki,** School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK, e-mail: kariukib@cardiff.ac.uk; and **Gamal A. El-Hiti,** Department of Optometry, College of Applied Medical Sciences, King Saud University, P.O. Box 10219, Riyadh 11433, Saudi Arabia, e-mail: gelhiti@ksu.edu.sa, gelhiti@hotmail.co.uk.
https://orcid.org/0000-0001-6675-3126
Obaid Fahad Aldosari: Department of Chemistry, College of Science and Human Studies at Hautat Sudair, Majmaah University, P.O. Box 66, 11952 Majmaah, Saudi Arabia; and Chemistry Department, College of Science and Humanities, Prince Sattam bin Abdulaziz University, P.O. Box 83, 11942 Alkharj, Saudi Arabia
Bakr F. Abdel-Wahab: Department of Chemistry, College of Science and Humanities, Shaqra University, Duwadimi, Saudi Arabia; and Applied Organic Chemistry Department, National Research Centre, Dokki, Giza, Egypt
Mohammad Hayal Alotaibi: National Center for Petrochemicals Technology, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia
Amany S. Hegazy: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK

CCDC no.: 1920908

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 × 0.31 × 0.11 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.17 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	29.9°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23341, 6338, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4290
$N(param)_{refined}$:	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 was 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).

Open Access. © 2019 Obaid Fahad Aldosari et al., published by De Gruyter. This work is licensed under the Creative Commons Attribution 4.0 Public License.

Brought to you by | Cardiff University
Authenticated
Download Date | 10/17/19 4:35 PM

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

Atom	x	y	z	U_{iso}*/U_{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	0.963043	0.298224	0.694212	0.099*
C3	0.88650(8)	0.3296(2)	0.71946(11)	0.0707(6)
H3	0.888562	0.423001	0.721373	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	0.806140	0.083814	0.738469	0.077*
C6	0.88153(8)	0.0535(2)	0.71168(11)	0.0729(6)
H6	0.879713	−0.039763	0.708661	0.087*
C7	0.79256(7)	0.34778(18)	0.75499(8)	0.0488(4)
H7	0.798013	0.442651	0.743769	0.059*
C8	0.78232(7)	0.33495(17)	0.82986(8)	0.0482(4)
H8	0.802710	0.258267	0.847596	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	0.703803	0.380208	0.985607	0.071*
H11B	0.695919	0.491112	0.931024	0.071*
C12	0.77351(8)	0.4304(2)	0.94189(9)	0.0672(5)
H12A	0.791400	0.351926	0.960474	0.081*
H12B	0.782137	0.506559	0.970309	0.081*
C13	0.79426(8)	0.4573(2)	0.87305(9)	0.0618(5)
H13A	0.777077	0.536315	0.854016	0.074*
H13B	0.832289	0.473463	0.875775	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	0.692416	0.262683	0.524876	0.065*
C17	0.62300(8)	0.30144(19)	0.47552(9)	0.0599(5)
H17	0.634909	0.280324	0.433596	0.072*
C18	0.57145(9)	0.3422(2)	0.48264(10)	0.0663(5)
H18	0.548504	0.347688	0.445733	0.080*
C19	0.55367(8)	0.3748(2)	0.54429(11)	0.0674(5)
H19	0.518598	0.401625	0.549265	0.081*
C20	0.58811(7)	0.3677(2)	0.59897(9)	0.0579(4)
H20	0.576329	0.392257	0.640500	0.070*
C21	0.65562(7)	0.21164(18)	0.89975(8)	0.0514(4)
H21	0.649726	0.154149	0.863912	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	0.609984	−0.006793	0.936419	0.073*
C24	0.57063(8)	0.0307(2)	1.01942(11)	0.0741(6)
H24	0.558494	−0.056440	1.026349	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	0.564940	0.328170	1.082367	0.094*
C27	0.60562(8)	0.2909(2)	0.99935(11)	0.0667(5)
H27	0.616705	0.379036	0.992620	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	0.654779	0.276486	0.684614	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]	0.535166	0.130659	0.661417	0.130*
C29[a]	0.5241(3)	0.1818(9)	0.8189(3)	0.120(2)
H29A[a]	0.525780	0.275315	0.830622	0.180*
H29B[a]	0.558754	0.142267	0.824413	0.180*
H29C[a]	0.499721	0.136374	0.846979	0.180*
C30[a]	0.4526(3)	0.1886(10)	0.7310(5)	0.154(4)
H30A[a]	0.451160	0.210382	0.684607	0.230*
H30B[a]	0.437535	0.260954	0.755692	0.230*
H30C[a]	0.432808	0.107590	0.738232	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)

[a]Occupancy: 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 planer 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.

Acknowledgements: The authors would like to thank the Deanship of Scientific Research at Majmaah University for supporting this work under Project Number No. 1440-127, and to Cardiff University for continued support.

References

1. Rigaku Oxford Diffraction: CrysAlis PRO. Rigaku Oxford Diffraction, Yarnton, England (2015).

Brought to you by | Cardiff University
Authenticated
Download Date | 10/17/19 4:35 PM

2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Faria, J. V.; Vegi, P. F.; Miguita, A. G. C.; Dos Santos, M. S.; Boechat, N.; Bernardino, A. M. R.: Recently reported biological activities of pyrazole compounds. Bioorg. Med. Chem. **25** (2017) 5891–5903.
6. Khan, M. F.; Alam, M. M.; Verma, G.; Akhtar, W.; Akhter, M.; Shaquiquzzaman, M.: The therapeutic voyage of pyrazole and its analogs: a review. Eur. J. Med. Chem. **120** (2016) 170–201.
7. Kumar, V.; Kaur, K.; Gupta, G. K.; Sharma, A. K.: Pyrazole containing natural products: synthetic preview and biological significance. Eur. J. Med. Chem. **69** (2013) 735–753.
8. Ding, Y.; Zhang, T.; Chen, Q.-Y.; Zhu, C.: Visible-light photocatalytic aerobic annulation for the green synthesis of pyrazoles. Org. Lett. **18** (2016) 4206–4209.
9. Maddila, S.; Jonnalagadda, S. B.; Gangu, K. K.; Maddila, S. N.: Recent advances in the synthesis of pyrazole derivatives using multicomponent reactions. Curr. Org. Synth. **14** (2017) 634–653.
10. Sun, A.; Ye, J.-H.; Yu, H.; Zhang, W.; Wang, X.: A new efficient synthesis of pyrazoles from hydrazonoyl halides and β-oxophosphonates. Tetrahedron Lett. **55** (2018) 889–892.
11. Gokhan-Kelekci, N.; Simsek, O. O.; Ercan, A.; Yelekci, K.; Sahin, Z. S.; Isik, S.; Ucar, G.; Bilgin, A. A.: Synthesis and molecular modeling of some novel hexahydroindazole derivatives as potent monoamine oxidase inhibitors. Bioorg. Med. Chem. **17** (2009) 6761–6772.

Brought to you by | Cardiff University
Authenticated
Download Date | 10/17/19 4:35 PM