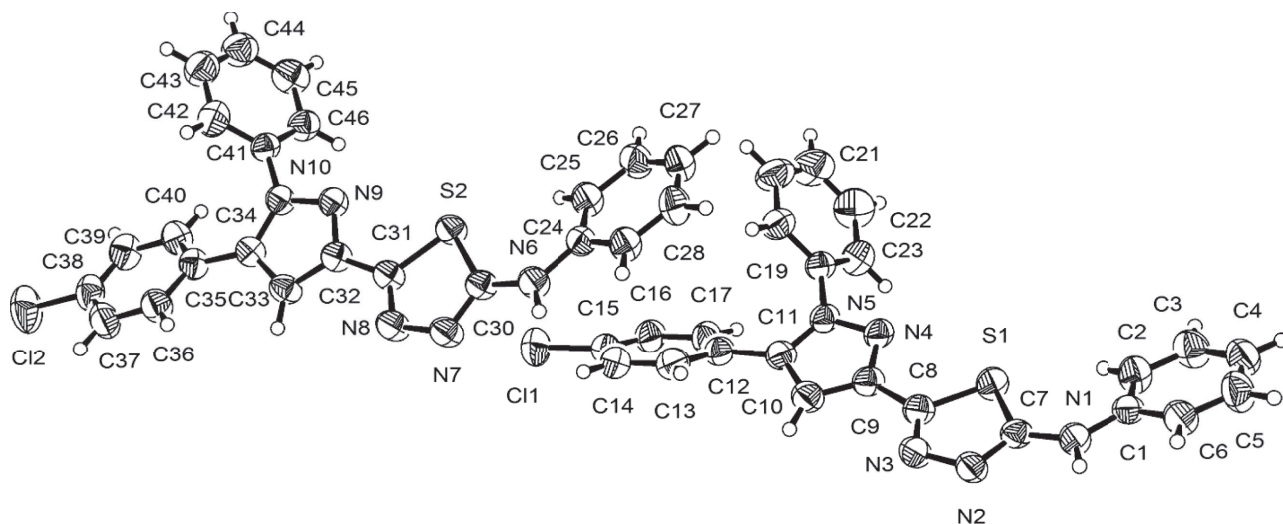


Gamal A. El-Hiti*, Bakr F. Abdel-Wahab, Amany S. Hegazy and Benson M. Kariuki

Crystal structure of 5-(5-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-3-yl)-*N*-phenyl-1,3,4-thiadiazol-2-amine, C₂₃H₁₆ClN₅S



DOI 10.1515/ncrs-2016-0259

Received August 26, 2016; accepted January 10, 2017; available online February 7, 2017

Abstract

C₂₃H₁₆ClN₅S, monoclinic, *P*₂₁/*n* (no. 14), *a* = 19.8348(9) Å, *b* = 8.8376(3) Å, *c* = 23.8486(10) Å, β = 97.646(4)°, *V* = 4143.3(3) Å³, *Z* = 8, *R*_{gt}(*F*) = 0.0492, *wR*_{ref}(*F*²) = 0.1276, *T* = 293(2) K.

CCDC no.: 1526218

The two crystallographically independent molecules of the title crystal structure are shown in the figure. Tables 1 and 2

contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.26 × 0.20 × 0.14 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	3.1 cm ^{−1}
Diffractometer, scan mode:	SuperNova, ω-scans
2θ _{max} , completeness:	59.8°, >84% (>99 up to 50°)
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	27827, 10183, 0.029
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 661
<i>N</i> (<i>param</i>) _{refined} :	523
Programs:	CrysAlis ^{PRO} [9], SHELX [10], ORTEP/WinGX [11]

*Corresponding author: Gamal A. El-Hiti, Cornea Research Chair, 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

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

Amany S. Hegazy and Benson M. Kariuki: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK

Source of material

The title compound was synthesized from treatment of 2-(5-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole-3-carbonyl)-*N*-phenylhydrazinecarbothioamide with concentrated sulfuric acid in an ice bath for 1 h. This reaction mixture was left to stir at room temperature overnight, poured into cooled water and then neutralized with an aqueous sodium hydroxide solution.

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	0.24211(11)	1.5782(2)	0.12747(8)	0.0460(5)
C2	0.22457(13)	1.5093(3)	0.17563(10)	0.0603(6)
H2	0.2315	1.4060	0.1811	0.072*
C3	0.19674(14)	1.5939(3)	0.21555(10)	0.0669(7)
H3	0.1856	1.5469	0.2480	0.080*
C4	0.18533(13)	1.7451(3)	0.20824(10)	0.0649(6)
H4	0.1659	1.8008	0.2351	0.078*
C5	0.20298(15)	1.8143(3)	0.16048(11)	0.0717(7)
H5	0.1956	1.9175	0.1552	0.086*
C6	0.23132(13)	1.7325(2)	0.12074(10)	0.0599(6)
H6	0.2434	1.7810	0.0889	0.072*
C7	0.29496(11)	1.3636(2)	0.08005(8)	0.0467(5)
C8	0.34536(11)	1.1181(2)	0.08771(9)	0.0489(5)
C9	0.37712(11)	0.9760(2)	0.10773(9)	0.0490(5)
C10	0.40845(12)	0.8662(2)	0.07793(10)	0.0554(5)
H10	0.4124	0.8657	0.0395	0.066*
C11	0.43206(11)	0.7591(2)	0.11730(9)	0.0489(5)
C12	0.46579(11)	0.6136(2)	0.10954(9)	0.0506(5)
C13	0.51383(12)	0.6040(3)	0.07242(10)	0.0598(6)
H13	0.5260	0.6904	0.0539	0.072*
C14	0.54393(13)	0.4663(3)	0.06270(11)	0.0647(6)
H14	0.5756	0.4601	0.0374	0.078*
C15	0.52673(13)	0.3407(3)	0.09049(10)	0.0617(6)
C16	0.47931(12)	0.3463(2)	0.12778(10)	0.0594(6)
H16	0.4680	0.2594	0.1464	0.071*
C17	0.44878(12)	0.4832(2)	0.13702(10)	0.0551(5)
H17	0.4165	0.4880	0.1619	0.066*
C18	0.43127(11)	0.7451(2)	0.22323(9)	0.0466(5)
C19	0.49753(12)	0.7012(3)	0.24166(10)	0.0587(6)
H19	0.5312	0.7125	0.2184	0.070*
C20	0.51278(16)	0.6402(3)	0.29527(12)	0.0760(8)
H20	0.5569	0.6087	0.3079	0.091*
C21	0.46357(18)	0.6261(3)	0.32967(13)	0.0869(9)
H21	0.4744	0.5856	0.3657	0.104*
C22	0.39786(17)	0.6715(3)	0.31134(12)	0.0820(8)
H22	0.3646	0.6630	0.3352	0.098*
C23	0.38130(13)	0.7297(3)	0.25744(11)	0.0600(6)
H23	0.3368	0.7581	0.2445	0.072*
C24	0.69815(10)	0.5923(2)	0.12635(8)	0.0453(5)
C25	0.69579(12)	0.5232(3)	0.17819(9)	0.0560(6)
H25	0.7009	0.4189	0.1817	0.067*
C26	0.68579(13)	0.6095(3)	0.22481(10)	0.0621(6)
H26	0.6850	0.5627	0.2597	0.075*
C27	0.67701(13)	0.7630(3)	0.22018(11)	0.0626(6)
H27	0.6704	0.8205	0.2517	0.075*
C28	0.67809(13)	0.8310(3)	0.16841(11)	0.0624(6)
H28	0.6715	0.9350	0.1649	0.075*
C29	0.68875(12)	0.7476(2)	0.12188(10)	0.0534(5)
H29	0.6897	0.7954	0.0872	0.064*
C30	0.72772(11)	0.3721(2)	0.06818(8)	0.0460(5)
C31	0.77591(11)	0.1258(2)	0.06346(8)	0.0464(5)
C32	0.81204(11)	−0.0165(2)	0.07216(8)	0.0455(5)
C33	0.82315(11)	−0.1264(2)	0.03206(9)	0.0503(5)
H33	0.8083	−0.1243	−0.0066	0.060*
C34	0.86055(11)	−0.2379(2)	0.06173(9)	0.0461(5)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C35	0.88346(11)	−0.3838(2)	0.04055(9)	0.0490(5)
C36	0.89623(12)	−0.3936(3)	−0.01508(10)	0.0598(6)
H36	0.8922	−0.3074	−0.0376	0.072*
C37	0.91496(13)	−0.5293(3)	−0.03778(11)	0.0665(7)
H37	0.9229	−0.5345	−0.0753	0.080*
C38	0.92168(12)	−0.6556(3)	−0.00414(12)	0.0615(6)
C39	0.90950(12)	−0.6500(3)	0.05095(11)	0.0616(6)
H39	0.9145	−0.7364	0.0734	0.074*
C40	0.88962(5)	−0.51452(10)	0.07312(4)	0.0558(6)
H40	0.8803	−0.5112	0.1103	0.067*
C41	0.90500(5)	−0.25945(10)	0.16613(4)	0.0451(5)
C42	0.97155(5)	−0.31118(10)	0.16891(4)	0.0659(6)
H42	0.9955	−0.2972	0.1383	0.079*
C43	1.00226(5)	−0.38380(10)	0.21739(4)	0.0781(8)
H43	1.0468	−0.4184	0.2193	0.094*
C44	0.96644(5)	−0.40469(10)	0.26307(4)	0.0771(8)
H44	0.9870	−0.4533	0.2955	0.093*
C45	0.89990(5)	−0.35295(10)	0.26029(4)	0.0706(7)
H45	0.8759	−0.3669	0.2909	0.085*
C46	0.86918(5)	−0.28033(10)	0.21181(4)	0.0555(5)
H46	0.8247	−0.2457	0.2099	0.067*
N1	0.26926(10)	1.50409(18)	0.08357(7)	0.0521(4)
H1	0.2696	1.5578	0.0535	0.062*
N2	0.31817(10)	1.31961(19)	0.03348(7)	0.0535(5)
N3	0.34769(10)	1.17836(19)	0.03870(7)	0.0553(5)
N4	0.38073(9)	0.94219(18)	0.16249(7)	0.0477(4)
N5	0.41448(9)	0.80814(18)	0.16768(7)	0.0461(4)
N6	0.70767(9)	0.51543(19)	0.07662(7)	0.0510(4)
H6A	0.6993	0.5686	0.0463	0.061*
N7	0.72575(10)	0.32082(19)	0.01643(7)	0.0545(5)
N8	0.75392(10)	0.17976(19)	0.01409(7)	0.0548(5)
N9	0.84089(9)	−0.05410(18)	0.12387(7)	0.0461(4)
N10	0.87069(9)	−0.18991(18)	0.11698(7)	0.0463(4)
S1	0.30460(3)	1.22919(6)	0.13349(2)	0.05229(15)
S2	0.76268(3)	0.24453(6)	0.11947(2)	0.04918(14)
Cl1	0.56410(4)	0.16672(9)	0.07866(3)	0.0902(3)
Cl2	0.94636(4)	−0.82648(8)	−0.03139(4)	0.0934(3)

The solid formed was filtered, dried and recrystallized from dimethylformamide to give needle-shaped colourless crystals of the title compound (Mp. 212–213 °C) [1].

Experimental details

All hydrogen atoms were placed in calculated positions and refined using a riding model. N–H bonds were fixed at 0.86 Å, with displacement parameters 1.2*U*_{eq}(N). Aromatic C–H distances were set to 0.93 Å and their *U*(iso) set to 1.2*U*_{eq} for the atoms to which they are bonded.

Discussion

1,3,4-Thiadiazole ring systems [2, 3] are present in a number of natural products and have a wide range of pharmacological

activities such as antibacterial, antifungal, anticancer, antioxidant and anticonvulsant [4–8].

The asymmetric unit comprises two molecules (I and II) of $C_{23}H_{16}ClN_5S$ with slightly different conformations. The twist angles about the bonds between the (phenylamino)-(thiadiazole)-(pyrazole)-(chlorophenyl) groups are $15.13(10)^\circ$, $10.49(13)^\circ$ and $39.56(10)^\circ$ respectively for one molecule and $22.11(7)^\circ$, $8.06(12)^\circ$ and $30.04(8)^\circ$ for the other molecule. The angle between the (pyrazole)-(phenyl) groups are $49.07(10)^\circ$ for I and $52.32(9)^\circ$ for II. Bond lengths and angles are all in the expected ranges. The two crystallographically independent molecules of the title crystal structure are pairwise connected by two $N-H \cdots N$ hydrogen bonds.

Acknowledgements: The project was supported by King Saud University, Deanship of Scientific Research, Research Chair.

References

1. Dawood, K. M.; Abdel-Gawad, H.; Mohamed, H. A.; Badria, F.: Synthesis, anti-HSV-1, and cytotoxic activities of some new pyrazole- and isoxazole-based heterocycles. *Med. Chem. Res.* **20** (2011) 912–917.
2. Hu, Y.; Li, C.-Y.; Wang, X.-M.; Yang, Y.-H.; Zhu, H.-L.: 1,3,4-Thiadiazole: synthesis, reactions, and applications in medicinal, agricultural, and materials chemistry. *Chem. Rev.* **114** (2014) 5572–5610.
3. Matysiak, J.: Biological and pharmacological activities of 1,3,4-thiadiazole based compounds. *Mini Rev. Med. Chem.* **15** (2015) 762–775.
4. Shawali, A. S.: 1,3,4-Thiadiazoles of pharmacological interest: recent trends in their synthesis *via* tandem 1,3-dipolar cycloaddition: review. *J. Adv. Res.* **5** (2014) 1–17.
5. Jain, A. K.; Sharma, S.; Vaidya, A.; Ravichandran, V.; Agrawal, R. K.: 1,3,4-thiadiazole and its derivatives: a review on recent progress in biological activities. *Chem. Biol. Drug Des.* **81** (2013) 557–576.
6. Ali, T. E.; El-Kazak, A. M.: Synthesis and antimicrobial activity of some new 1,3-thiazoles, 1,3,4-thiadiazoles, 1,2,4-triazoles and 1,3-thiazines incorporating acridine and 1,2,3,4-tetrahydroacridine moieties. *Eur. J. Chem.* **1** (2010) 6–11.
7. Li, S. H.; Li, G.; Huang, H. M.; Xiong, F.; Mai, X.; Kuang, B. H.; Liu, C. M.; Tu, G. G.: Synthesis of 1,3,4-thiadiazole derivatives as aminopeptidase N inhibitors. *Pharmazie* **64** (2009) 67–70.
8. Moise, M.; Sunel, V.; Profire, L.; Popa, M.; Desbrieres, J.; Peptu, C.: Synthesis and biological activity of some new 1,3,4-thiadiazole and 1,2,4-triazole compounds containing a phenylalanine moiety. *Molecules* **14** (2009) 2621–2631.
9. Agilent Technologies: CrysAlis^{PRO} Software system, version 1.171.37.35g, Agilent Technologies UK Ltd, Oxford, UK, (2014).
10. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
11. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.