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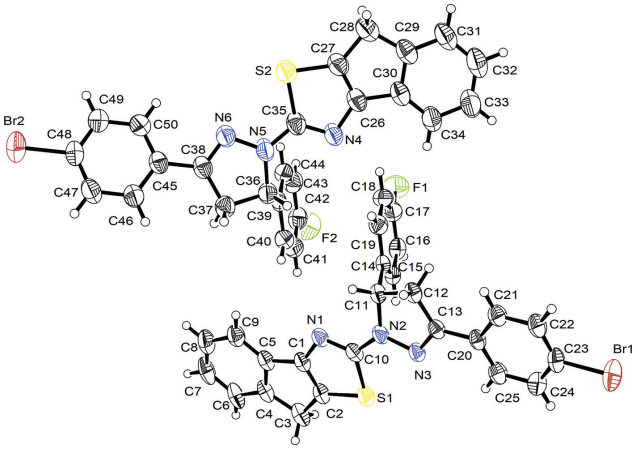
The crystal structure of 2-(3-(4-bromophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl)-8*H*-indeno[1,2-*d*]thiazole, $C_{25}H_{17}BrFN_3S$



https://doi.org/10.1515/ncrs-2020-0088
Received February 14, 2020; accepted March 10, 2020; available online April 9, 2020

Abstract

$C_{25}H_{17}BrFN_3S$, triclinic, $P\bar{1}$ (no. 2), $a = 11.2926(6)$ Å, $b = 11.5832(4)$ Å, $c = 16.9974(9)$ Å, $\alpha = 109.211(4)°$, $\beta = 90.211(4)°$, $\gamma = 95.290(4))°$, $V = 2089.21(18)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0580$, $wR_{ref}(F^2) = 0.1797$, $T = 296$ K.

CCDC no.: 1989338

The asymmetric unit of the title 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.

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Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.31 × 0.23 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.10 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	29.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18184, 9828, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5689
$N(param)_{refined}$:	559
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The title compound was synthesized from reaction of 3-(4-bromophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide (0.76 g, 2.0 mmol) and 2-bromo-2,3-dihydro-1*H*-inden-1-one (1.10 g, 2.0 mmol) in anhydrous ethanol (20 mL) under reflux for 2 h. The solid obtained was collected by filtration, washed with ethanol, dried, and recrystallized from dimethylformamide to give yellow crystals in 75% yield (Mp. 245–247 °C).

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses. The methine, methylene and aromatic ring hydrogens were idealized during refinement using options AFIX 13, AFIX 23 and AFIX 43 respectively in the SHELXL-2018 program [3]. The U_{iso} values of the hydrogen atoms were set to $1.2U_{eq}$(C).

Comment

Indeno[1,2-*d*]thiazoles act as A_1 adenosine receptor agonist allosteric enhancers [5] and anorectic agents [6]. Heterocycles containing pyrazole and thiazole moieties are biologically active and show some medicinal activities [7–9]. The most common synthetic methods for pyrazoles involve a treatment of 1,3-difunctional compounds with hydrazines [10], whereas thiazoles are commonly synthesized through Hantzsch, Gabriel, and Cook–Heilborn's syntheses [11]. Recently, the X-ray crystal structures of related compounds have been reported [12–15].

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.7847(3)	−0.9138(3)	−0.0235(3)	0.0449(9)
C2	0.7956(4)	−0.8662(3)	0.0605(3)	0.0496(10)
C3	0.8437(4)	−0.9531(4)	0.0985(3)	0.0579(11)
H3A	0.788957	−0.972712	0.137200	0.070*
H3B	0.920423	−0.920470	0.126766	0.070*
C4	0.8542(3)	−1.0631(3)	0.0213(3)	0.0520(10)
C5	0.8177(3)	−1.0398(3)	−0.0506(3)	0.0474(9)
C6	0.8937(4)	−1.1753(4)	0.0138(4)	0.0643(13)
H6	0.919225	−1.191634	0.060814	0.077*
C7	0.8949(4)	−1.2640(4)	−0.0648(4)	0.0711(15)
H7	0.922093	−1.339470	−0.070144	0.085*
C8	0.8570(4)	−1.2415(4)	−0.1334(4)	0.0684(13)
H8	0.857739	−1.302330	−0.185239	0.082*
C9	0.8165(4)	−1.1285(4)	−0.1280(3)	0.0589(11)
H9	0.789733	−1.113843	−0.175317	0.071*
C10	0.7353(3)	−0.7322(3)	−0.0106(3)	0.0449(9)
C11	0.6999(3)	−0.6294(3)	−0.1168(2)	0.0426(9)
H11	0.651597	−0.700770	−0.154705	0.051*
C12	0.6363(3)	−0.5129(3)	−0.1024(3)	0.0450(9)
H12A	0.674895	−0.460110	−0.130728	0.054*
H12B	0.553341	−0.532903	−0.121040	0.054*
C13	0.6487(3)	−0.4542(3)	−0.0097(2)	0.0414(8)
C14	0.8228(3)	−0.6187(3)	−0.1503(2)	0.0397(8)
C15	0.9256(3)	−0.6046(3)	−0.1016(3)	0.0448(9)
H15	0.919675	−0.603527	−0.046835	0.054*
C16	1.0366(4)	−0.5920(3)	−0.1335(3)	0.0524(10)
H16	1.105346	−0.581839	−0.100666	0.063*
C17	1.0431(4)	−0.5949(4)	−0.2139(3)	0.0565(11)
C18	0.9436(4)	−0.6092(4)	−0.2647(3)	0.0587(11)
H18	0.950311	−0.611258	−0.319593	0.070*
C19	0.8335(4)	−0.6205(4)	−0.2313(3)	0.0515(10)
H19	0.765123	−0.629463	−0.264292	0.062*
C20	0.6190(3)	−0.3308(3)	0.0363(3)	0.0414(8)
C21	0.5708(3)	−0.2606(3)	−0.0061(3)	0.0488(9)
H21	0.560032	−0.292225	−0.063754	0.059*
C22	0.5388(4)	−0.1444(4)	0.0365(3)	0.0543(11)
H22	0.506645	−0.098061	0.007864	0.065*
C23	0.5551(4)	−0.0989(3)	0.1210(3)	0.0527(10)
C24	0.6058(4)	−0.1638(4)	0.1653(3)	0.0557(10)
H24	0.618604	−0.130090	0.222721	0.067*
C25	0.6370(4)	−0.2798(4)	0.1224(3)	0.0513(10)
H25	0.670611	−0.324748	0.151575	0.062*
C26	0.7911(4)	−0.6370(4)	−0.4978(3)	0.0595(11)
C27	0.7786(4)	−0.6799(4)	−0.5812(3)	0.0616(12)
C28	0.8099(5)	−0.5818(4)	−0.6194(3)	0.0730(14)
H28A	0.743381	−0.571018	−0.651702	0.088*
H28B	0.878197	−0.599197	−0.654405	0.088*
C29	0.8386(4)	−0.4718(4)	−0.5418(3)	0.0660(13)
C30	0.8279(4)	−0.5048(4)	−0.4691(3)	0.0596(11)
C31	0.8733(5)	−0.3507(5)	−0.5342(4)	0.0815(17)
H31	0.881020	−0.327248	−0.581403	0.098*
C32	0.8962(5)	−0.2651(5)	−0.4559(4)	0.0879(18)
H32	0.920104	−0.183921	−0.451072	0.105*
C33	0.8846(5)	−0.2968(5)	−0.3847(4)	0.0892(17)
H33	0.899697	−0.237443	−0.332498	0.107*
C34	0.8502(5)	−0.4185(4)	−0.3917(4)	0.0738(14)
H34	0.842377	−0.441041	−0.344131	0.089*
C35	0.7345(4)	−0.8260(4)	−0.5101(3)	0.0583(11)
C36	0.6952(4)	−0.9366(4)	−0.4054(3)	0.0540(10)
H36	0.649351	−0.871964	−0.370693	0.065*
C37	0.6235(4)	−1.0623(4)	−0.4234(3)	0.0584(11)
H37A	0.660165	−1.112115	−0.395987	0.070*
H37B	0.542251	−1.053572	−0.405905	0.070*
C38	0.6285(4)	−1.1162(4)	−0.5166(3)	0.0532(10)
C39	0.8161(4)	−0.9272(3)	−0.3643(3)	0.0472(9)
C40	0.8226(4)	−0.9273(4)	−0.2831(3)	0.0561(11)
H40	0.752743	−0.932860	−0.255177	0.067*
C41	0.9309(4)	−0.9194(4)	−0.2426(3)	0.0599(11)
H41	0.934775	−0.919487	−0.187980	0.072*
C42	1.0308(4)	−0.9116(4)	−0.2846(3)	0.0608(11)
C43	1.0302(4)	−0.9117(4)	−0.3645(3)	0.0626(12)
H43	1.101001	−0.906769	−0.391531	0.075*
C44	0.9214(4)	−0.9192(4)	−0.4045(3)	0.0535(10)
H44	0.918958	−0.918875	−0.459169	0.064*
C45	0.5863(4)	−1.2433(4)	−0.5670(3)	0.0522(10)
C46	0.5211(4)	−1.3196(4)	−0.5316(3)	0.0631(12)
H46	0.506257	−1.291512	−0.475032	0.076*
C47	0.4778(5)	−1.4382(4)	−0.5803(3)	0.0705(13)
H47	0.431153	−1.488225	−0.557087	0.085*
C48	0.5042(4)	−1.4803(4)	−0.6624(3)	0.0598(11)
C49	0.5717(5)	−1.4096(4)	−0.6979(3)	0.0724(14)
H49	0.590483	−1.440813	−0.753709	0.087*
C50	0.6126(5)	−1.2908(4)	−0.6507(3)	0.0677(13)
H50	0.658327	−1.241867	−0.675138	0.081*
N1	0.7501(3)	−0.8388(3)	−0.0660(2)	0.0454(8)
N2	0.7015(3)	−0.6367(3)	−0.0326(2)	0.0472(8)
N3	0.6834(3)	−0.5267(3)	0.0282(2)	0.0428(7)
N4	0.7652(3)	−0.7184(3)	−0.4544(2)	0.0593(9)
N5	0.7018(4)	−0.9287(3)	−0.4898(2)	0.0659(11)
N6	0.6692(3)	−1.0389(3)	−0.5523(2)	0.0569(9)
Br1	0.51139(5)	0.06048(4)	0.18048(4)	0.0835(2)
Br2	0.44554(6)	−1.64283(5)	−0.72785(4)	0.0974(2)
S1	0.76099(10)	−0.71559(9)	0.09420(7)	0.0530(3)
S2	0.73495(12)	−0.83545(11)	−0.61521(8)	0.0671(3)
F1	1.1517(2)	−0.5866(3)	−0.2468(2)	0.0849(9)
F2	1.1384(3)	−0.8993(3)	−0.2442(2)	0.0937(10)

The asymmetric unit of the title structure consists of two independent molecules (see the figure). The molecule comprises indenothiazolyl (**A$_1$**[C1—C10,N1,S1] and **A$_2$**[C26—C35,N4,S2]), pyrazolyl (**B$_1$**[C11—C13,N2,N3] and **B$_2$**[C36—C38,N5,N6]), bromophenyl (**C$_1$**[C20—C25,Br1] and **C$_2$**[C45—C50,Br2]) and fluorophenyl (**D$_1$**[C14—C19,F1] and **D$_2$**[C39—C44,F2]) ring systems. In both molecules, ring systems **A**, **B** and **C** are almost coplanar with twist angles **A$_1$**/**B$_1$** = 6.63(15)° and **B$_1$**/**C$_1$** = 7.48(18)° for one molecule and **A$_2$**/**B$_2$** = 11.13(21)° and **B$_2$**/**C$_2$** = 14.35(20)° for the other molecule. The interplanar angle between the fluorophenyl and pyrazolyl rings are

$\mathbf{B_1}/\mathbf{D_1} = 71.64(13)°$ and $\mathbf{B_2}/\mathbf{D_2} = 66.35(15)°$. In the crystal, a number of rings are involved in $\pi\cdots\pi$ interactions. The rings of the fluorophenyl groups of one type of molecule are parallel with a $\mathbf{D_2}\cdots\mathbf{D_2}$ centroid separation of 3.62 Å. The indenothiazolyl groups are also parallel with centroid separations $\mathbf{A_1}\cdots\mathbf{A_1} = 4.18$ Å and $\mathbf{A_2}\cdots\mathbf{A_2} = 4.21$ Å. The indenothiazolyl group of one molecule and the bromophenyl group of the other are also parallel with $\mathbf{A_1}\cdots\mathbf{C_1}$ a centroid separation of 4.15 Å. Two molecules of one type are linked by a pair of C16—H16$\cdots$N3 contacts.

Acknowledgements: The authors are grateful to the Deanship of Scientific Research, King Saud University for funding through Vice Deanship of Scientific Research Chairs.

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