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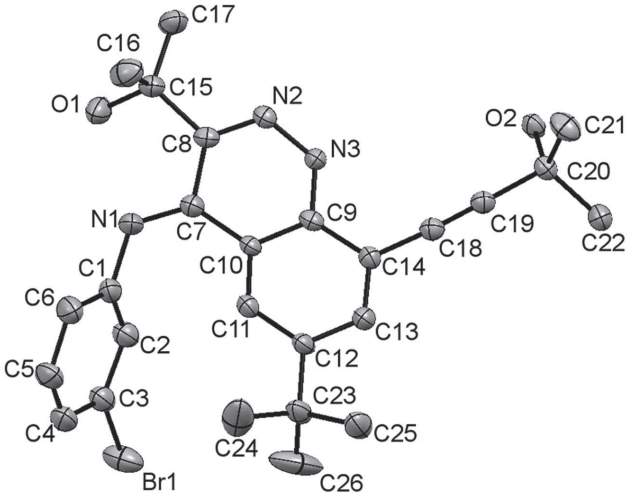
Crystal structure of 4-(4-((3-bromophenyl)amino)-6-(*tert*-butyl)-3-(2-hydroxypropan-2-yl)cinnolin-8-yl)-2-methylbut-3-yn-2-ol, $C_{26}H_{30}BrN_3O_2$



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Abstract

$C_{26}H_{30}BrN_3O_2$, triclinic, $P\bar{1}$ (no. 2), $a = 12.257(3)$ Å, $b = 12.451(3)$ Å, $c = 17.325(3)$ Å, $\alpha = 92.05(3)°$, $\beta = 107.04(3)°$, $\gamma = 93.96(3)°$, $V = 2517.5(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0722$, $wR_{ref}(F^2) = 0.1929$, $T = 173(2)$ K.

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One of two molecules of the asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Orange plate
	Size 0.16 × 0.14 × 0.04 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	16.6 cm^{-1}
Diffractometer, scan mode:	Saturn 724, ω at fixed $\chi = 45°$
$2\theta_{max}$, completeness:	51°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	28966, 9336, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7908
$N(param)_{refined}$:	592
Programs:	SHELX [5], CrystalClear [6]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.69755(5)	0.09543(4)	0.61078(3)	0.05245(19)
Br1A	0.83683(5)	0.57930(5)	0.54202(3)	0.0677(2)
O1	0.1623(2)	0.0960(3)	0.29907(18)	0.0422(8)
H1	0.1992	0.0462	0.3228	0.063*
O2A	0.6703(2)	0.2274(2)	−0.06517(15)	0.0268(6)
H2A	0.6207	0.2607	−0.0518	0.040*
N1	0.3822(3)	0.1812(3)	0.3446(2)	0.0347(8)
H1B	0.3119	0.1977	0.3396	0.042*
N1A	0.5305(3)	0.6930(3)	0.28265(19)	0.0279(7)
H1A	0.4674	0.7267	0.2684	0.033*
N2	0.3052(3)	−0.0094(3)	0.17515(18)	0.0240(7)
N2A	0.4546(3)	0.4683(3)	0.13016(19)	0.0275(7)
N3	0.4085(3)	−0.0388(3)	0.17496(18)	0.0237(7)
N3A	0.5547(3)	0.4443(3)	0.12276(19)	0.0266(7)
C1	0.4702(3)	0.2205(4)	0.4159(2)	0.0327(9)
C1A	0.6112(3)	0.7262(3)	0.3583(2)	0.0264(8)
C2	0.5318(4)	0.1506(4)	0.4679(2)	0.0350(9)
H2	0.5185	0.0750	0.4555	0.042*
C2A	0.6723(3)	0.6504(3)	0.4058(2)	0.0321(9)
H2AA	0.6589	0.5760	0.3888	0.039*
C3	0.6141(4)	0.1913(4)	0.5391(3)	0.0369(10)
C3A	0.7533(4)	0.6849(4)	0.4785(3)	0.0377(10)
C4	0.6343(4)	0.3012(4)	0.5569(3)	0.0422(11)
H4	0.6902	0.3288	0.6054	0.051*
C4A	0.7732(4)	0.7920(4)	0.5052(3)	0.0419(11)
H4A	0.8298	0.8147	0.5547	0.050*
C5	0.5742(4)	0.3690(4)	0.5052(3)	0.0418(11)
H5	0.5908	0.4446	0.5169	0.050*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C5A	0.7088(4)	0.8650(4)	0.4583(3)	0.0431(12)
H5A	0.7199	0.9389	0.4766	0.052*
C6	0.4880(4)	0.3316(4)	0.4349(3)	0.0425(11)
H6	0.4427	0.3803	0.4010	0.051*
C6A	0.6280(4)	0.8336(4)	0.3847(3)	0.0344(9)
H6A	0.5848	0.8855	0.3530	0.041*
C7	0.3996(3)	0.1226(3)	0.2865(2)	0.0282(8)
C7A	0.5421(3)	0.6131(3)	0.2296(2)	0.0228(8)
C8	0.2986(3)	0.0680(3)	0.2255(2)	0.0238(8)
C8A	0.4460(3)	0.5480(3)	0.1821(2)	0.0242(8)
C9	0.5093(3)	0.0182(3)	0.2173(2)	0.0233(8)
C9A	0.6508(3)	0.5047(3)	0.1661(2)	0.0240(8)
C10	0.5091(3)	0.1025(3)	0.2728(2)	0.0226(7)
C10A	0.6492(3)	0.5941(3)	0.2181(2)	0.0241(8)
C11	0.6118(3)	0.1654(3)	0.3107(2)	0.0262(8)
H11	0.6105	0.2257	0.3455	0.031*
C11A	0.7521(3)	0.6609(3)	0.2534(2)	0.0253(8)
H11A	0.7494	0.7254	0.2835	0.030*
C12	0.7149(3)	0.1425(3)	0.2991(2)	0.0274(8)
C12A	0.8547(3)	0.6349(3)	0.2453(2)	0.0259(8)
C13	0.7132(3)	0.0546(3)	0.2454(2)	0.0280(8)
H13	0.7836	0.0360	0.2381	0.034*
C13A	0.8566(3)	0.5393(3)	0.1989(2)	0.0261(8)
H13A	0.9283	0.5177	0.1962	0.031*
C14	0.6140(3)	−0.0059(3)	0.2028(2)	0.0238(8)
C14A	0.7590(3)	0.4771(3)	0.1581(2)	0.0257(8)
C15	0.1784(3)	0.0993(3)	0.2204(2)	0.0295(9)
C15A	0.3254(3)	0.5563(3)	0.1897(2)	0.0268(8)
C16	0.1637(4)	0.2129(4)	0.1914(3)	0.0447(11)
H16D	0.0858	0.2314	0.1869	0.067*
H16E	0.1769	0.2161	0.1384	0.067*
H16F	0.2190	0.2641	0.2301	0.067*
C16A	0.3189(4)	0.5050(4)	0.2671(3)	0.0366(10)
H16A	0.3759	0.5430	0.3137	0.055*
H16B	0.3345	0.4290	0.2644	0.055*
H16C	0.2422	0.5100	0.2728	0.055*
C17	0.0854(3)	0.0207(4)	0.1662(3)	0.0385(10)
H17D	0.0957	−0.0521	0.1854	0.058*
H17E	0.0898	0.0217	0.1107	0.058*
H17F	0.0103	0.0418	0.1676	0.058*
C17A	0.2330(3)	0.5038(3)	0.1164(3)	0.0326(9)
H17A	0.1573	0.5170	0.1214	0.049*
H17B	0.2401	0.4259	0.1136	0.049*
H17C	0.2420	0.5346	0.0672	0.049*
C18	0.6116(3)	−0.0879(3)	0.1419(2)	0.0249(8)
C18A	0.7635(3)	0.3847(3)	0.1068(2)	0.0278(8)
C19	0.6044(3)	−0.1525(3)	0.0882(2)	0.0261(8)
C19A	0.7702(3)	0.3106(3)	0.0636(2)	0.0275(8)
C20	0.5946(3)	−0.2313(3)	0.0200(2)	0.0237(8)
C20A	0.7683(3)	0.2194(3)	0.0056(2)	0.0260(8)
C21	0.5671(4)	−0.1764(4)	−0.0597(2)	0.0372(10)
H21D	0.5573	−0.2305	−0.1042	0.056*
H21E	0.6300	−0.1228	−0.0587	0.056*
H21F	0.4962	−0.1406	−0.0676	0.056*
C21A	0.8747(3)	0.2284(4)	−0.0232(3)	0.0363(10)
H21A	0.8679	0.1716	−0.0654	0.054*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H21B	0.9426	0.2202	0.0225	0.054*
H21C	0.8819	0.2992	−0.0450	0.054*
C22	0.7053(3)	−0.2878(3)	0.0334(2)	0.0313(9)
H22D	0.7236	−0.3205	0.0858	0.047*
H22E	0.7681	−0.2349	0.0327	0.047*
H22F	0.6951	−0.3440	−0.0098	0.047*
C22A	0.7555(4)	0.1117(3)	0.0419(3)	0.0385(10)
H22A	0.6825	0.1048	0.0544	0.058*
H22B	0.8187	0.1078	0.0915	0.058*
H22C	0.7571	0.0531	0.0030	0.058*
C23	0.8273(3)	0.2081(4)	0.3455(3)	0.0353(10)
C23A	0.9663(3)	0.7045(3)	0.2855(2)	0.0314(9)
C24	0.8062(5)	0.3222(5)	0.3711(4)	0.072(2)
H24D	0.7597	0.3565	0.3239	0.107*
H24E	0.8797	0.3650	0.3936	0.107*
H24F	0.7656	0.3181	0.4121	0.107*
C24A	0.9444(4)	0.8161(4)	0.3155(4)	0.0653(18)
H24A	0.8935	0.8512	0.2706	0.098*
H24B	1.0172	0.8604	0.3362	0.098*
H24C	0.9083	0.8081	0.3587	0.098*
C25	0.9073(4)	0.2212(4)	0.2929(3)	0.0446(12)
H25D	0.9322	0.1508	0.2818	0.067*
H25E	0.9742	0.2702	0.3214	0.067*
H25F	0.8667	0.2512	0.2419	0.067*
C25A	1.0364(4)	0.7203(4)	0.2263(3)	0.0501(13)
H25A	1.0588	0.6504	0.2112	0.075*
H25B	1.1052	0.7685	0.2520	0.075*
H25C	0.9902	0.7521	0.1778	0.075*
C26	0.8840(5)	0.1492(6)	0.4194(3)	0.075(2)
H26D	0.8318	0.1397	0.4525	0.113*
H26E	0.9545	0.1911	0.4511	0.113*
H26F	0.9024	0.0783	0.4026	0.113*
C26A	1.0349(5)	0.6445(5)	0.3571(3)	0.0642(16)
H26A	0.9886	0.6299	0.3936	0.096*
H26B	1.1050	0.6890	0.3863	0.096*
H26C	1.0551	0.5763	0.3372	0.096*
O1A	0.3055(2)	0.6683(2)	0.19970(16)	0.0287(6)
H1AA	0.3059	0.6994	0.1575	0.043*
O2	0.5014(2)	−0.3088(2)	0.02006(16)	0.0271(6)
H2B	0.4803	−0.3513	−0.0213	0.041*

Source of material

All solvents and reagents for synthesis were purchased from commercial sources and used without further purification. 2,6-Bis(3-methyl-3-hydroxyl-1-butynyl)-4-tert-butylaniline was prepared according to reference [1]. To a stirred MeOH solution (5 mL) of 2,6-bis(3-methyl-3-hydroxyl-1-butynyl)-4-tert-butylaniline (0.626 g, 2 mmol) was added slowly conc. HCl (2.5 mL). The reaction mixture was kept at 273 K. An aqueous solution (1 mL) of $NaNO_2$ (151.8 mg, 2.2 mmol) was added dropwise to generate the azonium intermediate, and the reaction mixture was stirred for 10 min. A solution of

3-bromoaniline (0.260 g, 2.2 mmol) and sodium hydroxide (0.150 g) in MeOH-H_2O (2:1, *v*/*v*, 9 mL) was kept at 273 K. With stirring, the azonium intermediate was added dropwise to the 3-bromoaniline solution while maintaining the temperature at 273 K. After stirring for 2 h at room temperature, water (50 mL) was added to induce precipitation of an orange solid, which was isolated by filtration and washed with water, and dried. Flash column chromatography on silica gel, eluted with hexane-EtOAc (5:1, *v*/*v*), gives a solid (513.3 mg, yield 51.7%) which was recrystallized from acetone to give orange plates.

Experimental details

H atoms were included in calculated positions and refined using a riding model, with C—H distances, O—H distances, N—H distances constrained to 0.95–0.98 Å, 0.84 Å and 0.88 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

Cinnoline derivatives are an important class of heterocyclic compounds showing important biological activities [2]. In recent years, a large number of cinnoline compounds were found to own interesting pharmacological properties including anticancer [3], anti-inflammatory and antibacterial [4].

There are two crystallographically independent molecules in the asymmetric unit, which are slightly different concerning their conformation. All bond lengths and angles are in the expected ranges. There are intramolecular hydrogen bonding N—H···O interactions and intermolecular hydrogen bonding O—H···O and weak O—H···Br interactions in the crystal structure.

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