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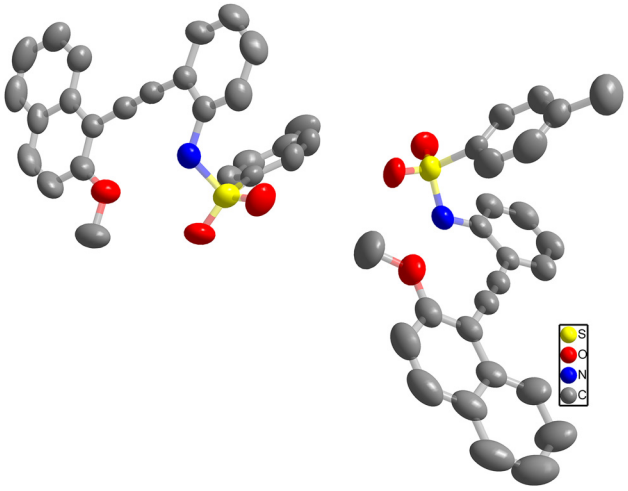
The crystal structure of *N*-(2-((2-methoxynaphthalen-1-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide, $C_{26}H_{21}NO_3S$



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Abstract

$C_{26}H_{21}NO_3S$, triclinic, $P\bar{1}$ (no. 2), a = 11.7598(11) Å, b = 12.7434(12) Å, c = 17.0020(16) Å, α = 104.146(3)°, β = 103.926(3)°, γ = 102.322(3)°, V = 2295.5(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0453, $wR_{ref}(F^2)$ = 0.1320, T = 293 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.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.23 × 0.22 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.17 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX II, φ and ω
θ_{max}, completeness:	25.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	39,850, 8079, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 6321
$N(param)_{refined}$:	563
Programs:	Bruker[1], SHELX[2]

1 Source of materials

Under nitrogen atmosphere, compound 2-bromoaniline (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%) were dissolved in DMF:Et_3N = 2:1 (0.5 M). Then 1-ethynyl-2-methoxynaphthalene (1.3 equiv) was added. The resulting mixture was stirred overnight at 100 °C. After the reaction was completed (monitored by TLC), the reaction was cooled to room temperature and quenched with brine. The reaction system was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The mixture was purified by flash column chromatography (PE/EA) to afford the coupling product. The mixture of corresponding *p*–toluenesulfonyl chloride (1.1 equiv) and coupling product (1.0 equiv) in pyridine (0.2 M) was stirred overnight at room temperature. After completion of the reaction (monitored by TLC), the mixture was treated with HCl (1 M) and extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. *N*-(2-((2-methoxynaphthalen-1-yl)ethynyl)phenyl)benzenesulfonamide was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent.

2 Experimental details

In the title compound, all non-hydrogen atoms were refined anisotropically. All hydrogen atomic positions were taken from a difference Fourier map. Hydrogen atoms were

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.80937 (5)	0.16743 (6)	0.77196 (4)	0.07764 (19)
O1	0.72443 (16)	0.23059 (18)	0.78364 (13)	0.1029 (6)
O2	0.82841 (16)	0.13506 (18)	0.69079 (10)	0.0997 (6)
O3	0.63512 (15)	0.19113 (14)	0.95462 (11)	0.0838 (5)
N1	0.75941 (15)	0.05387 (17)	0.79694 (12)	0.0757 (5)
H1	0.687409	0.038380	0.802376	0.091*
C1	1.2984 (3)	0.4069 (3)	1.0429 (2)	0.1282 (12)
H1A	1.322276	0.352396	1.068387	0.192*
H1B	1.291717	0.468175	1.085718	0.192*
H1C	1.358723	0.435408	1.018127	0.192*
C2	1.1755 (2)	0.3511 (2)	0.97394 (15)	0.0757 (6)
C3	1.1689 (2)	0.3036 (2)	0.89101 (15)	0.0775 (6)
H3	1.240697	0.308919	0.876361	0.093*
C4	1.05830 (19)	0.2483 (2)	0.82889 (14)	0.0691 (5)
H4	1.055764	0.216234	0.772906	0.083*
C5	0.95132 (18)	0.24040 (18)	0.84956 (12)	0.0608 (5)
C6	0.9550 (2)	0.2883 (2)	0.93253 (15)	0.0809 (7)
H6	0.883039	0.283803	0.946923	0.097*
C7	1.0666 (3)	0.3428 (2)	0.99346 (15)	0.0890 (7)
H7	1.069366	0.375172	1.049454	0.107*
C8	0.83308 (17)	−0.02029 (17)	0.80995 (13)	0.0619 (5)
C9	0.8870 (2)	−0.0645 (2)	0.75009 (15)	0.0784 (6)
H9	0.876660	−0.045511	0.699887	0.094*
C10	0.9559 (2)	−0.1364 (2)	0.76562 (18)	0.0857 (7)
H10	0.992920	−0.164776	0.725954	0.103*
C11	0.9707 (2)	−0.1667 (2)	0.83834 (18)	0.0824 (7)
H11	1.016530	−0.216129	0.847474	0.099*
C12	0.91777 (19)	−0.12410 (17)	0.89802 (15)	0.0686 (5)
H12	0.927980	−0.144965	0.947425	0.082*
C13	0.84875 (16)	−0.04963 (15)	0.88492 (12)	0.0552 (4)
C14	0.79321 (17)	−0.00368 (16)	0.94622 (13)	0.0573 (4)
C15	0.74220 (17)	0.03768 (16)	0.99269 (13)	0.0579 (5)
C16	0.67446 (16)	0.08334 (16)	1.04478 (13)	0.0578 (5)
C17	0.66239 (18)	0.04733 (17)	1.11624 (13)	0.0631 (5)
C18	0.7243 (2)	−0.0265 (2)	1.14434 (16)	0.0802 (6)
H18	0.775020	−0.053840	1.115416	0.096*
C19	0.7109 (3)	−0.0583 (3)	1.21336 (19)	0.1054 (9)
H19	0.754159	−0.105563	1.231814	0.126*
C20	0.6329 (4)	−0.0207 (3)	1.2566 (2)	0.1136 (10)
H20	0.623384	−0.044007	1.302962	0.136*
C21	0.5713 (3)	0.0494 (3)	1.23109 (18)	0.0972 (9)
H21	0.518971	0.073330	1.259942	0.117*
C22	0.5850 (2)	0.08720 (19)	1.16136 (14)	0.0742 (6)
C23	0.5262 (2)	0.1631 (2)	1.13523 (18)	0.0863 (8)
H23	0.475026	0.189261	1.164238	0.104*
C24	0.5416 (2)	0.1998 (2)	1.06887 (18)	0.0833 (7)
H24	0.502471	0.251505	1.053962	0.100*
C25	0.61625 (18)	0.16000 (18)	1.02262 (14)	0.0673 (5)
C26	0.5777 (3)	0.2707 (3)	0.9287 (2)	0.1184 (11)
H26A	0.595754	0.281649	0.878665	0.178*
H26B	0.608094	0.341448	0.973847	0.178*
H26C	0.490774	0.242375	0.916314	0.178*
S2	0.32466 (5)	0.34449 (5)	0.70728 (3)	0.06694 (16)
O4	0.41174 (16)	0.37760 (15)	0.78986 (9)	0.0865 (5)
O5	0.20180 (15)	0.28064 (15)	0.69260 (11)	0.0891 (5)
O6	0.02397 (15)	0.33713 (14)	0.52382 (11)	0.0818 (4)
N2	0.31268 (15)	0.45876 (14)	0.68166 (11)	0.0631 (4)
H2	0.244486	0.475272	0.674068	0.076*
C27	0.5326 (4)	0.1082 (3)	0.4469 (2)	0.1214 (11)
H27A	0.470486	0.043226	0.405653	0.182*
H27B	0.600270	0.085077	0.473888	0.182*
H27C	0.560103	0.160913	0.418828	0.182*
C28	0.4804 (3)	0.1638 (2)	0.51332 (16)	0.0793 (7)
C29	0.3572 (3)	0.1575 (2)	0.49290 (16)	0.0888 (7)
H29	0.305725	0.115699	0.438152	0.107*
C30	0.3091 (2)	0.2114 (2)	0.55158 (15)	0.0790 (6)
H30	0.226400	0.207013	0.536400	0.095*
C31	0.38486 (18)	0.27226 (16)	0.63331 (12)	0.0576 (5)
C32	0.5076 (2)	0.27845 (19)	0.65505 (14)	0.0691 (5)
H32	0.558880	0.318698	0.710122	0.083*
C33	0.5538 (2)	0.2247 (2)	0.59467 (16)	0.0794 (6)
H33	0.636710	0.229854	0.609567	0.095*
C34	0.41636 (17)	0.53057 (15)	0.67206 (12)	0.0550 (4)
C35	0.5244 (2)	0.58038 (19)	0.73839 (14)	0.0723 (6)
H35	0.530095	0.569038	0.791026	0.087*
C36	0.6241 (2)	0.6470 (2)	0.72665 (17)	0.0816 (7)
H36	0.697022	0.679346	0.771333	0.098*
C37	0.6169 (2)	0.66592 (19)	0.65011 (18)	0.0820 (7)
H37	0.684771	0.710716	0.642909	0.098*
C38	0.50989 (19)	0.61907 (17)	0.58407 (15)	0.0709 (6)
H38	0.505123	0.633220	0.532417	0.085*
C39	0.40768 (17)	0.55013 (15)	0.59354 (12)	0.0546 (4)
C40	0.29467 (18)	0.49983 (16)	0.52608 (12)	0.0565 (4)
C41	0.19491 (18)	0.45610 (16)	0.47549 (12)	0.0572 (4)
C42	0.07296 (17)	0.40789 (15)	0.41822 (12)	0.0566 (4)
C43	0.04114 (18)	0.42648 (15)	0.33730 (12)	0.0588 (5)
C44	0.1281 (2)	0.48654 (18)	0.30732 (13)	0.0699 (5)
H44	0.210427	0.511779	0.339386	0.084*
C45	0.0922 (3)	0.5078 (2)	0.23158 (16)	0.0878 (7)
H45	0.150134	0.547721	0.212657	0.105*
C46	−0.0313 (3)	0.4699 (3)	0.18221 (17)	0.1011 (9)
H46	−0.054912	0.486411	0.131433	0.121*
C47	−0.1159 (3)	0.4100 (3)	0.20762 (17)	0.0954 (9)
H47	−0.197112	0.383859	0.173326	0.114*
C48	−0.0836 (2)	0.38563 (18)	0.28594 (14)	0.0723 (6)
C49	−0.1689 (2)	0.3240 (2)	0.3151 (2)	0.0889 (8)
H49	−0.250187	0.295203	0.280954	0.107*
C50	−0.1369 (2)	0.3050 (2)	0.3913 (2)	0.0844 (7)
H50	−0.195961	0.262969	0.408236	0.101*
C51	−0.01494 (19)	0.34856 (17)	0.44487 (15)	0.0664 (5)
C52	−0.0647 (3)	0.2903 (2)	0.5599 (2)	0.1028 (9)
H52A	−0.104259	0.212216	0.527336	0.154*
H52B	−0.124601	0.331073	0.558781	0.154*
H52C	−0.024833	0.296042	0.617768	0.154*

assigned with common isotropic displacement factors U_{iso}(H) = 1.2 times U_{eq} (C, phenyl ring and methylene carbon) and U_{iso}(H) = 1.5 times U_{eq} (C, methyl carbon). All the H atoms were refined as riding on their parent atom.

3 Comment

Aromatic alkynes, as highly active organic synthesis intermediates, have been widely studied. In recent years, many reactions involving addition, substitution, coupling, and polymerization involving aromatic alkynes have been reported and widely applied in biology, new drugs, and functional materials.[3–5] The strong conjugated structure of aromatic rings makes aromatic alkynes and their derivatives more unstable than general substituted alkynes,[6] making them more prone to form carbon negative ions and exhibiting high reactivity.[7] The intramolecular cyclization of alkynes is an effective method for constructing various heterocycles,[8] intramolecular cyclization has been widely studied due to its ability to synthesize special structural cores, which always start from bifunctional substrates.[9] And ortho alkynylbenzamide is one of the important and useful bifunctional structural units, which can synthesize various heterocyclic compounds through regioselective cyclization of triple bonds.[10] The construction of ortho alkynylbenzamide is regarded as a desirable and valuble synthetic goal,[11] which would be of great significance to the synthetic and pharmaceutical fields.[12]

There are two crystallographically independent molecules in the asymmetric unit (see the Figure). The title compound contains one naphthalene and one ethynylaniline. The dihedral angles of ring 1 (C8–C9–C10–C11–C12–C13) and naphthalene is 10.8°, indicating that these rings are almost coplanar. The dihedral angles of ring 2 (C2–C3–C4–C5–C6–C7) and ring 1 (C8–C9–C10–C11–C12–C13), ring 2 (C2–C3–C4–C5–C6–C7) and naphthalene are 63.3° and 68.4°, And the torsion angles of C13–C14–C15–C16 are −58.2°, the angles of C13–C14–C15 and C14–C15–C16 are 174.9° and 176.7°. The short bond distance between C14 and C15 indicates the presence of triple bonds. All the bond lengths and angles are comparable with their analogues and in the expected ranges.[13–19]

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *APEX2*, *SAINT and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2004.
2. Sheldrick, G. M. Crystal Structure Refifinement with *SHELXL*. *Acta Crystallogr. Sect. C* **2015**, *C71*, 3–8.
3. Escorihuela, J.; Lledós, A.; Ujaque, G. Anti-Markovnikov Intermolecular Hydroamination of Alkenes and Alkynes: A Mechanistic View. *Chem. Rev.* **2023**, *123*, 9139–9203.
4. Li, G.; Huo, X.; Jiang, X.; Zhang, W. Asymmetric Synthesis of Allylic Compounds via Hydrofunctionalisation and Difunctionalisation of Dienes, Allenes, and Alkynes. *Chem. Soc. Rev.* **2020**, *49*, 2060–2118.
5. Trost, B. M.; Van Vranken, D. L. Asymmetric Transition Metal-Catalyzed Allylic Alkylations. *Chem. Rev.* **1996**, *96*, 395–422.
6. Grugel, C. P.; Breit, B. Rhodium-Catalyzed Enantioselective Cyclization of 3-Allenyl-Indoles: Access to Functionalized Tetrahydrocarbazoles. *Org. Lett.* **2019**, *21*, 5798–5802.
7. Li, Y.; Liou, Y.-C.; Chen, X.; Ackermann, L. Thioether-Enabled Palladium-Catalyzed Atroposelective C–H Olefination for N–C and C–C Axial Chirality. *Chem. Sci.* **2022**, *13*, 4088–4094.
8. Boyarskiy, V. P.; Ryabukhin, D. S.; Bokach, N. A.; Vasilyev, A. V. Alkenylation of Arenes and Heteroarenes with Alkynes. *Chem. Rev.* **2016**, *116*, 5894–5986.
9. Pirnot, M. T.; Wang, Y. M.; Buchwald, S. L. Copper Hydride Catalyzed Hydroamination of Alkenes and Alkynes. *Angew. Chem. Int. Ed.* **2016**, *55*, 48–57.
10. Grugel, C. P.; Breit, B. Rhodium-Catalyzed Enantioselective Decarboxylative Alkynylation of Allenes with Arylpropiolic Acids. *Org. Lett.* **2018**, *20*, 1066–1069.
11. He, L.; Nie, H.; Qiu, G.; Gao, Y.; Wu, J. 2-Alkynylbenzaldoxime: A Versatile Building Block for the Generation of *N*-Heterocycles. *Org. Biomol. Chem.* **2014**, *12*, 9045–9053.
12. Liu, Z.-S.; Deng, S.; Gao, Q.; Hua, Y.; Cheng, H.-G.; Qi, X.; Zhou, Q. Construction of Axially Chiral Biaryls via Atroposelective Ortho-C–H Arylation of Aryl Iodides. *ACS Catal*. **2023**, *13*, 2968–2980.
13. Yang, M. J.; Men, J.; Ma, X. Y.; Yi, S. X.; Gao, G. W. 5-(2-Phenylethynyl) Isobenzofuran-1,3-Dione. *Acta Crystallogr.* **2008**, *E64*, 2193.
14. Hua, B. L.; Lu, L.; Xiao, Y. M.; Guo, W. G. Crystal Structure of Dimethyl 4-(Phenylethynyl)Phthalate, $C_{18}H_{14}O_4$. *Z. Kristallogr. N. Cryst. Struct.* **2012**, *227*, 117–118.
15. Li, H.-B.; Chen, L.-Y.; Jiang, H.; Ma, X.-Y.; Gao, G.-W. Crystal Structure of 1,5-Di(4-(2-Methylbut-3-Yn-2-Ol))-Naphthalene, $C_{20}H_{20}O_2$. *Z. Kristallogr. N. Cryst. Struct.* **2014**, *229*, 397–398.

16. Pu, X.; Meng, F.; Zhang, S. The Crystal Structure of [1-(4-(Trifluoromethyl)Phenyl)-3,4-Dihydroquinolin-2(1*h*)-One], $C_{16}H_{12}F_3NO$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 857–859.
17. Wang, G.; Zhang, N.; Yan, B.-X.; Zhang, Z.-W.; Li, S.-W.; Luo, G.; Ye, Z.-S. Ligand-Exchange-Enabled Axially Chiral Recognition in Asymmetric Aminopalladation/Olefination of 2-Alkynylanilides. *ACS Catal*. **2024**, *14*, 4053–4065.
18. Gorelik, T. E.; Ulmer, A.; Schleper, A. L.; Kuehne, A. J. C. Crystal Structure of 9,10-Bis-((Perchloro-Phenyl)-Ethynyl)Anthracene Determined from Three-Dimensional Electron Diffraction Data. *Z. Kristallogr. Cryst. Mater.* **2023**, *238*, 253–260.
19. Jia, S.; Tian, Y.; Li, X.; Wang, P.; Lan, Y.; Yan, H. Atroposelective Construction of Nine-Membered Carbonate-Bridged Biaryls. *Angew. Chem. Int. Ed.* **2022**, *61*, e202206501.