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Crystal structure of *N,N*-dimethyl-4-((7-nitrobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)aniline, $C_{16}H_{12}N_4O_2S$

Table 1: Data collection and handling.

Crystal:	Black plate
Size:	0.21 × 0.13 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.24 mm ⁻¹
Diffractometer, scan mode:	Saturn724+, φ and ω
$\theta_{\max}$, completeness:	26.4°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5799, 2934, 0.042
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2472
$N(\text{param})_{\text{refined}}$:	210
Programs:	CrystalClear [1], Olex2 [2], SHELX [3, 4]

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Abstract

$C_{16}H_{12}N_4O_2S$, triclinic, $P\bar{1}$ (no. 2), $a = 7.249(2)$ Å, $b = 8.265(3)$ Å, $c = 12.786(4)$ Å, $\alpha = 82.449(11)^\circ$, $\beta = 75.210(10)^\circ$, $\gamma = 83.977(11)^\circ$, $V = 732.3(4)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0669$, $wR_{\text{ref}}(F^2) = 0.1726$, $T = 173.15$ 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.

Source of material

The title compound was obtained by the Sonogashira cross-coupling reaction of 4-ethynyl-*N,N*-dimethylbenzenamine and 4-bromo-7-nitrobenzo[c][1,2,5]thiadiazole with

$PdCl_2(PPh_3)_2$ and CuI under an argon flow at room temperature. The compound was purified by SiO_2 chromatography with CH_2Cl_2 /petroleum ether (1/2, v/v).

Single crystals suitable for X-ray diffraction were obtained by crystallization of the title compound from dichloromethane and *n*-hexane.

Experimental details

The hydrogen atoms were placed with common isotropic displacement factors $U_{\text{iso}}(H) = 1.2$ times $U_{\text{eq}}(C, \text{aromatic ring})$. The final refinement succeeded using geometrical restraints, with $C-H = 0.95$ Å.

Comment

Push-pull chromophores with strong electron donors connected by π -conjugated spacers to strong electron acceptors have been studied due to their high optoelectronic susceptibility and architectural flexibility and structural feature [5–9]. 2,1,3-Benzothiadiazole is an important building block of optoelectronic devices due to its large reduction potential and electron affinity [9–13]. A mount of molecular materials containing this unit as electron-accepting moiety are widely exploited for their applications in nonlinear optics [14–16]. This molecule is linked through phenylethynyl conjugated bridges with *N,N*-dimethylbenzenamine as the donor and nitrobenzothiadiazole as the acceptor and has great potential for developing controlled nonlinear optical materials. A view on the structure of the title molecule is shown in the figure.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
S1	0.93964(14)	0.23550(11)	0.50555(7)	0.0384(3)
O1	1.0952(4)	−0.1625(3)	0.7334(2)	0.0425(7)
O2	0.9728(4)	−0.1677(3)	0.9057(2)	0.0466(7)
N1	1.0055(4)	−0.0977(3)	0.8120(2)	0.0297(6)
N2	0.9868(4)	0.0910(3)	0.5953(2)	0.0323(7)
N3	0.8498(4)	0.3801(3)	0.5814(2)	0.0337(7)
N4	0.3081(4)	1.3577(3)	0.7563(2)	0.0366(7)
C2	0.9299(4)	0.1519(4)	0.6911(2)	0.0257(7)
C12	0.3868(5)	1.1996(4)	0.7561(3)	0.0281(7)
C1	0.9328(4)	0.0725(4)	0.7967(3)	0.0266(7)
C4	0.7824(5)	0.4054(4)	0.7773(3)	0.0294(7)
C3	0.8515(5)	0.3181(4)	0.6832(3)	0.0272(7)
C7	0.7072(5)	0.5716(4)	0.7659(3)	0.0326(8)
C6	0.8642(5)	0.1558(4)	0.8860(3)	0.0309(7)
H6	0.864831	0.101175	0.956123	0.037*
C9	0.5523(5)	0.8731(4)	0.7562(3)	0.0303(7)
C11	0.4621(5)	1.1277(4)	0.6580(3)	0.0316(7)
H11	0.457294	1.189834	0.590661	0.038*
C14	0.4757(5)	0.9428(4)	0.8531(3)	0.0305(7)
H14	0.479979	0.879611	0.920267	0.037*
C13	0.3938(5)	1.1014(4)	0.8539(3)	0.0320(7)
H13	0.341472	1.144765	0.921344	0.038*
C16	0.2487(5)	1.4337(4)	0.8575(3)	0.0354(8)
H16A	0.155679	1.367805	0.910815	0.053*
H16B	0.189991	1.544123	0.843645	0.053*
H16C	0.360592	1.440124	0.886149	0.053*
C5	0.7925(5)	0.3207(4)	0.8763(3)	0.0324(8)
H5	0.749620	0.375393	0.940044	0.039*
C10	0.5420(5)	0.9693(4)	0.6586(3)	0.0317(8)
H10	0.591228	0.924074	0.591566	0.038*
C8	0.6377(5)	0.7094(4)	0.7583(3)	0.0334(8)
C15	0.3180(6)	1.4627(4)	0.6552(3)	0.0408(9)
H15A	0.452211	1.476864	0.617918	0.061*
H15B	0.251511	1.569607	0.670751	0.061*
H15C	0.256922	1.412620	0.608591	0.061*

The unit cell contains one molecule of the title compound, which is synthesized under controlled conditions with Sonogashira cross-coupling reaction.

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References

1. Rigaku. CrystalClear. Rigaku Corporation, Tokyo, Japan (2007).
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
3. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Sheldrick, G. M.: Crystal structure refinement with SHELX. *Acta Crystallogr.* **C71** (2015) 3–8.
5. Chen, S. H.; Chen, N.; Yan, Y. L.; Liu, T. F.; Yu, Y. W.; Li, Y. J.; Liu, H. B.; Zhao, Y. S.; Li, Y. L.: Controlling growth of molecular crystal aggregates for efficient optical waveguides. *Chem. Commun.* **48** (2012) 9011–9013.
6. Qian, H.; Cousins, M. E.; Horak, E. H.; Wakefield, A.; Liptak, M. D.; Aprahamian, I.: Suppression of Kasha's rule as a mechanism for fluorescent molecular rotors and aggregation-induced emission. *Nat. Chem.* **9** (2017) 83–87.
7. Xu, J.; Zheng, H.; Liu, H.; Zhou, C.; Zhao, Y.; Li, Y.; Li, Y.: Crystal hierarchical supramolecular architectures from 1-D precursor single-crystal seeds. *J. Phys. Chem. C* **114** (2010) 2925–2931.
8. Chen, S. H.; Qin, Z. H.; Liu, T. F.; Wu, X. Z.; Li, Y. J.; Liu, H. B.; Song, Y. L.; Li, Y. L.: Aggregation-induced emission on benzothiadiazole dyads with large third-order optical nonlinearity. *Phys. Chem. Chem. Phys.* **15** (2013) 12660–12666.
9. Yang, J.; Chen, S.: Crystal structure of 2-(4-(dimethylamino)phenyl)-10-methylacridin-9(10H)-one, C₂₂H₂₀N₂O. *Z. Kristallogr. NCS* **234** (2019) 187–188.
10. Xu, J.; Liu, X.; Lv, J.; Zhu, M.; Huang, C.; Zhou, W.; Yin, X.; Liu, H.; Li, Y.; Ye, H.: Morphology transition and aggregation-induced emission of an intramolecular charge-transfer compound. *Langmuir* **24** (2008) 4231–4237.
11. Xiong, J.; Wang, K.; Yao, Z.; Zou, B.; Xu, J.; Bu, X.-H.: Multi-stimuli-responsive fluorescence switching from a pyridine-functionalized tetraphenylethene AIEgen. *ACS Appl. Mater. Interfaces* **10** (2018) 5819–5827.
12. Chen, S.; Yang, J.: Crystal structure of 2-bromo-7-(4-(dimethylamino)phenyl)-10-methylacridin-9(10H)-one, C₂₂H₁₉BrN₂O. *Z. Kristallogr. NCS* **234** (2019) 71–72.
13. Xu, J.; Semin, S.; Cremers, J.; Wang, L.; Savoini, M.; Fron, E.; Coutino, E.; Chervy, T.; Wang, C.; Li, Y.: Controlling micro-sized polymorphic architectures with distinct linear and nonlinear optical properties. *Adv. Opt. Mater.* **3** (2015) 948–956.
14. Chen, Y. C.; Lam, J. W. Y.; Kwok, R. T. K.; Liu, B.; Tang, B. Z.: Aggregation-induced emission: fundamental understanding and future developments. *Mater. Horiz.* **6** (2019) 428–433.
15. Chen, S.; Qin, Z.; Liu, T.; Wu, X.; Li, Y.; Liu, H.; Song, Y.; Li, Y.: Aggregation-induced emission on benzothiadiazole dyads with large third-order optical nonlinearity. *Phys. Chem. Chem. Phys.* **15** (2013) 12660–12666.
16. Ju, C.; Zhou, Y.; Semin, S.; Yang, G.; Tinnemans, P.; Duan, Y.; Feng, Y.; Rasing, T.; Xu, J.: Solvent dependent linear and nonlinear optical properties of triphenylamine unit incorporated difluoroboron β-diketone complexes. *Dyes Pigm.* **162** (2019) 776–785.