

# Synthesis, crystal structure and Hirshfeld surface analysis of (3*Z*)-4-[(4-amino-1,2,5-oxadiazol-3-yl)-amino]-3-bromo-1,1,1-trifluorobut-3-en-2-one

Firudin I. Guseinov,<sup>a,b</sup> Sevim Türktekin Çelikesir,<sup>c</sup> Mehmet Akkurt,<sup>c</sup> Viacheslav O. Ovsyannikov,<sup>b,d</sup> Bogdan I. Ugrak,<sup>b</sup> Oksana M. Lavrova,<sup>b</sup> Aida I. Samigullina<sup>b</sup> and Ajaya Bhattarai<sup>e\*</sup>

Received 24 April 2024

Accepted 3 May 2024

Edited by B. Therrien, University of Neuchâtel, Switzerland

**Keywords:** crystal structure;  $\alpha$ -haloketone; diaminofurazan; non-covalent interactions; oxadiazole ring; disorder; Hirshfeld surface analysis.

**CCDC reference:** 2352897

**Supporting information:** this article has supporting information at journals.iucr.org/e

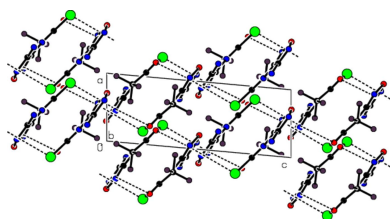
<sup>a</sup>Kosygin State University of Russia, 117997 Moscow, Russian Federation, <sup>b</sup>N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation, <sup>c</sup>Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Türkiye, <sup>d</sup>MIREA, Russian Technology University, Lomonosov Institute of Fine Chemical Technology, Moscow, 119571, Russian Federation, and <sup>e</sup>Department of Chemistry, M.M.A.M.C (Tribhuvan University), Biratnagar, Nepal. \*Correspondence e-mail: ajaya.bhattarai@mmamc.tu.edu.np

In the title compound, C<sub>6</sub>H<sub>4</sub>BrF<sub>3</sub>N<sub>4</sub>O<sub>2</sub>, the oxadiazole ring is essentially planar with a maximum deviation of 0.003 (2) Å. In the crystal, molecular pairs are connected by N—H···N hydrogen bonds, forming dimers with an *R*<sub>2</sub><sup>2</sup>(8) motif. The dimers are linked into layers parallel to the (10 $\bar{4}$ ) plane by N—H···O hydrogen bonds. In addition, C—O··· $\pi$  and C—Br··· $\pi$  interactions connect the molecules, forming a three-dimensional network. The F atoms of the trifluoromethyl group are disordered over two sites in a 0.515 (6): 0.485 (6) ratio. The intermolecular interactions in the crystal structure were investigated and quantified using Hirshfeld surface analysis.

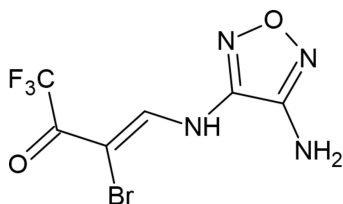
## 1. Chemical context

Among the main trends in the development of organic chemistry over the past 20 years, one can note the key role and rapid development of the chemistry of organofluorine compounds (Meanwell, 2018). This is due to the extremely high practical importance of organofluorine molecules. The introduction of fluorine into the target molecule changes such important parameters as lipophilicity, solubility, binding to receptors, metabolism, acid–base characteristics, and conformational properties of compounds. Currently, about 25% of new drugs and 35% of substances used in agriculture (agrochemicals) contain at least one fluorine atom (Chandra *et al.*, 2023; Han *et al.*, 2020; Mei *et al.*, 2019; Shabir *et al.*, 2023; Zhang *et al.*, 2022).

Diaminofurazanes and their derivatives are widely used to obtain useful heterocyclic compounds, high-energy explosives with great potential application value, antimicrobials, highly effective biocidal and antitumor agents, as well as in photochemistry (Chang *et al.*, 2023; Chen *et al.*, 2022; Dutta *et al.*, 2022; Liao *et al.*, 2020; Liu *et al.*, 2022; Ugrak *et al.*, 2023). Similarly to other *N*-ligands (Gurbanov *et al.*, 2022*a,b*; Kopylovich *et al.*, 2011*a,b*, 2012), new derivatives of furazan can also be used in crystal engineering (Gurbanov *et al.*, 2020) as well as the synthesis of coordination compounds for catalysis (Mac Leod *et al.*, 2012; Mahmudov *et al.*, 2013; Mizar *et al.*, 2012) and biological studies (Martins *et al.*, 2017). In fact, the non-covalent bond-acceptor ability of the furazan motif can be employed as a unique tool for crystal engineering. We believe that the combination of trifluoromethyl and furazan fragments in one molecule can lead to the synthesis of new compounds



with useful properties. Therefore, we studied the condensation of (*Z*)-3-bromo-4-ethoxy-1,1,1-trifluorobut-3-en-2-one with diaminofurazan in different polar solvents, with the best yield being in ethanol. It was shown that the reaction occurs only with the participation of the vinyl fragment and the active ketone group is not affected. The condensation product is an enamine, and its structure was confirmed by NMR spectroscopy and X-ray diffraction analysis.

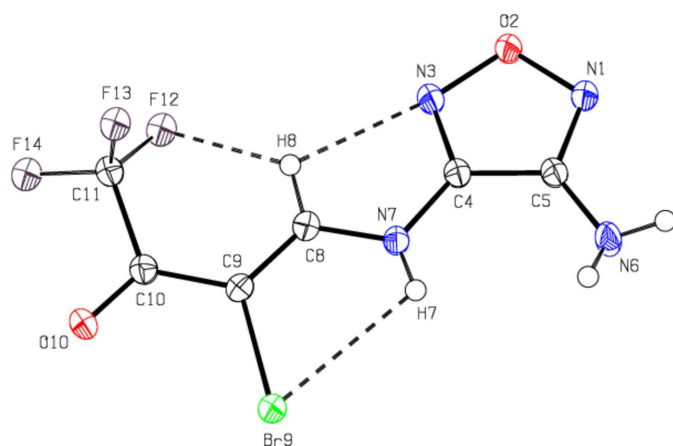


## 2. Structural commentary

In the title compound (Fig. 1), the oxadiazole ring (N1/O2/N3/C4/C5) is essentially planar [maximum deviation = 0.003 (2) Å for C4]. In the molecule, the intramolecular N—H···Br, C—H···F and C—H···N hydrogen bonds form *S*(5), *S*(6) and *S*(5) ring motifs, respectively (Bernstein *et al.*, 1995; Table 1; Fig. 1). The N3—C4—N7—C8, C4—N7—C8—C9, C8—C9—C10—O10 and C8—C9—C10—C11 torsion angles are  $-7.5$  (4),  $173.0$  (2),  $-178.3$  (2) and  $-2.8$  (4)°, respectively. The geometric parameters are normal and comparable to those of related compounds listed in the *Database survey* section.

## 3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecular pairs are connected by N—H···N hydrogen bonds, forming dimers with an  $R_2^2(8)$  motif (Bern-



**Figure 1**  
Molecular structure of the title compound, showing the atom-labeling scheme and with displacement ellipsoids drawn at the 50% probability level. The intramolecular N—H···Br, C—H···F and C—H···N hydrogen bonds are shown as dashed lines. Only the major disorder component is shown for clarity.

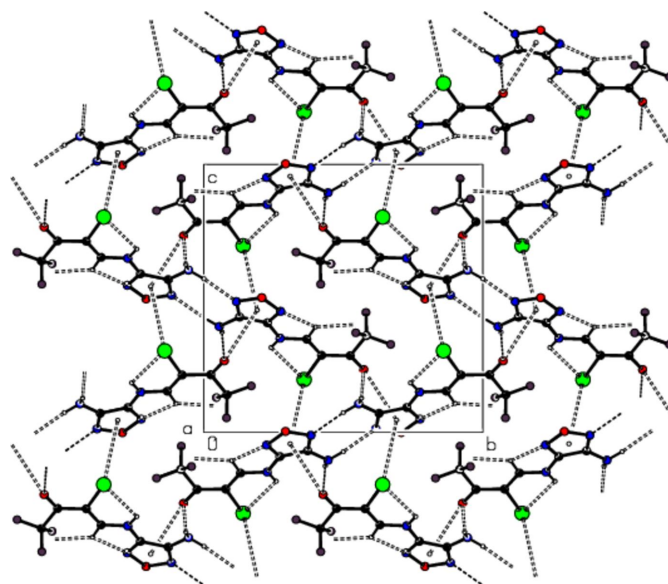
**Table 1**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N6—H6 <i>A</i> ···O10 <sup>i</sup>	0.77 (4)	2.14 (4)	2.871 (3)	159 (4)
N6—H6 <i>B</i> ···N1 <sup>ii</sup>	0.90 (4)	2.11 (4)	2.995 (3)	169 (3)
N7—H7···Br9	0.81 (3)	2.76 (3)	3.127 (2)	109 (2)
C8—H8···F12	0.95 (3)	2.17 (3)	2.799 (5)	123 (2)
C8—H8···F12 <i>A</i>	0.95 (3)	2.11 (3)	2.808 (5)	129 (2)
C8—H8···N3	0.95 (3)	2.38 (3)	2.759 (3)	103.3 (19)

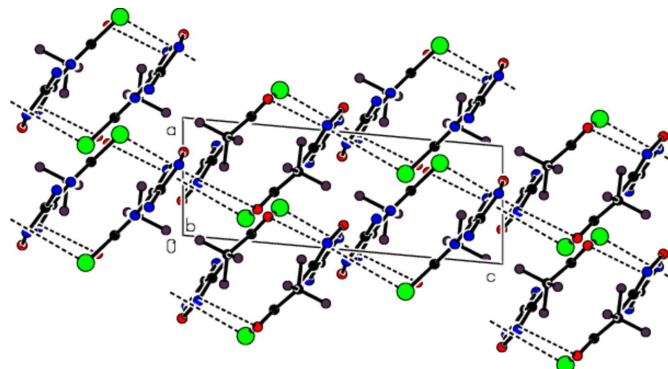
Symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 2, -y, -z + 1$ .

stein *et al.*, 1995; Table 1; Fig. 2). The dimers are linked into layers parallel to the (10 $\bar{4}$ ) plane by N—H···O hydrogen bonds (Table 1; Fig. 2). In addition, C—O··· $\pi$  and C—Br··· $\pi$  interactions connect the molecules, forming a three-dimensional network (Figs. 2 and 3).

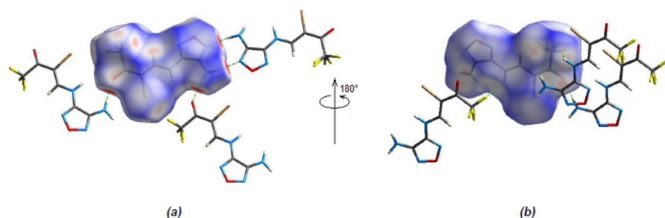
To quantify the intermolecular interactions, a Hirshfeld surface analysis was performed and *CrystalExplorer17.5*



**Figure 2**  
Views of the intramolecular N—H···Br, C—H···F, C—H···N hydrogen bonds, the intermolecular N—H···O, N—H···N hydrogen bonds, and the C—O··· $\pi$  and C—Br··· $\pi$  interactions along the *a*-axis.

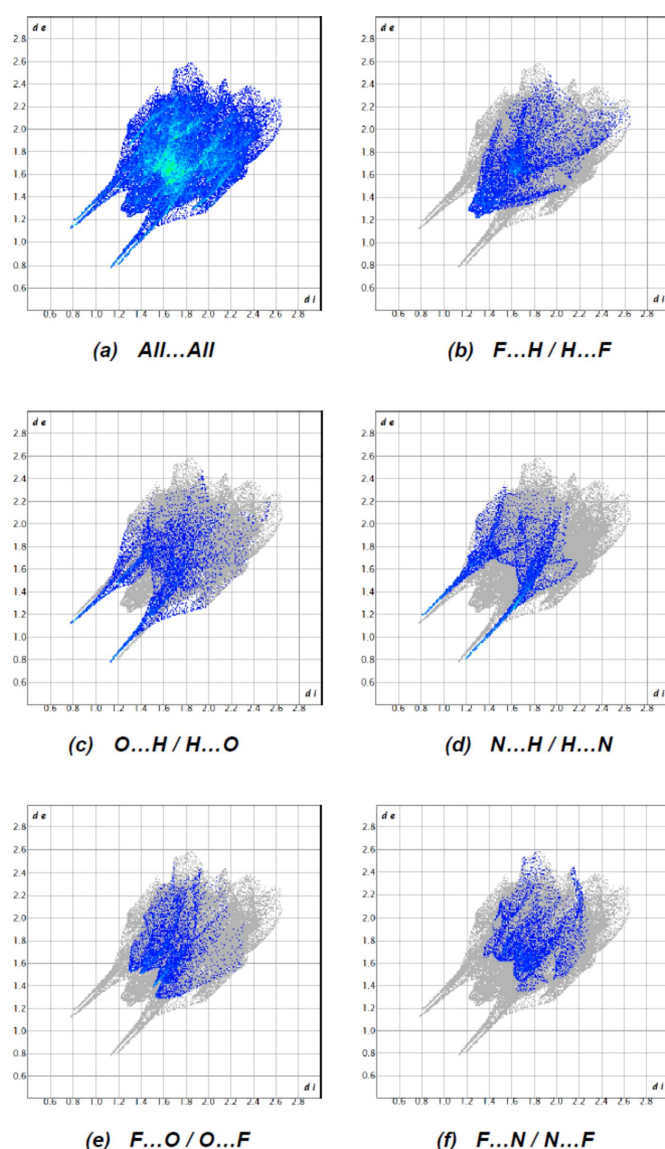


**Figure 3**  
Packing viewed along the *b*-axis with the C—O··· $\pi$  and C—Br··· $\pi$  interactions indicated by dashed lines.



**Figure 4**  
The three-dimensional Hirshfeld surface for the title compound, plotted over  $d_{\text{norm}}$ .

(Spackman *et al.*, 2021) was used to obtain two-dimensional fingerprint plots. Fig. 4 shows the Hirshfeld surface mapped over  $d_{\text{norm}}$  using a common surface resolution and a constant



**Figure 5**  
A view of the two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b)  $\text{F}\cdots\text{H}/\text{H}\cdots\text{F}$ , (c)  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ , (d)  $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ , (e)  $\text{F}\cdots\text{O}/\text{O}\cdots\text{F}$ , and (f)  $\text{F}\cdots\text{N}/\text{N}\cdots\text{F}$  interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

color scale of  $-0.5339$  (red) to  $+0.9642$  (blue) a.u. On the Hirshfeld surface, shorter and longer contacts are indicated by red and blue spots, respectively, and contacts with lengths about equal to the sum of the van der Waals radii are indicated by white spots.

Fig. 5 depicts the two-dimensional fingerprint plots of ( $d_i$ ,  $d_e$ ) points from all contacts contributing to the Hirshfeld surface analysis in normal mode for all atoms. The most important intermolecular interactions are  $\text{F}\cdots\text{H}/\text{H}\cdots\text{F}$ ,  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$  and  $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$  contacts, contributing to 12.8%, 11.9% and 10.7%, respectively, to the overall crystal packing. Other interactions and their respective contributions are  $\text{F}\cdots\text{O}/\text{O}\cdots\text{F}$  (8.8%),  $\text{F}\cdots\text{N}/\text{N}\cdots\text{F}$  (7.4%),  $\text{F}\cdots\text{F}$  (6.3%),  $\text{Br}\cdots\text{H}/\text{H}\cdots\text{Br}$  (5.7%),  $\text{Br}\cdots\text{F}/\text{F}\cdots\text{Br}$  (5.2%),  $\text{F}\cdots\text{C}/\text{C}\cdots\text{F}$  (4.9%),  $\text{Br}\cdots\text{C}/\text{C}\cdots\text{Br}$  (4.5%),  $\text{Br}\cdots\text{O}/\text{O}\cdots\text{Br}$  (3.8%),  $\text{Br}\cdots\text{N}/\text{N}\cdots\text{Br}$  (3.5%),  $\text{O}\cdots\text{C}/\text{C}\cdots\text{O}$  (3.4%),  $\text{N}\cdots\text{C}/\text{C}\cdots\text{N}$  (3.1%),  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$  (3.0%),  $\text{O}\cdots\text{N}/\text{N}\cdots\text{O}$  (2.3%),  $\text{H}\cdots\text{H}$  (2.2%) and  $\text{N}\cdots\text{N}$  (0.4%).

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom *et al.*, 2016) gave four compounds closely related to the title compounds, *viz.* CSD refcodes KIMZEP (**I**: Okmanov *et al.*, 2023), KIMZIT (**II**: Okmanov *et al.*, 2023), ZARJEJ (**III**: Jia *et al.*, 2012) and PUHDUS (**IV**: Zhang *et al.*, 2009).

In the crystals of **I** and **II**,  $\text{C}-\text{H}\cdots\pi$  interactions are observed between neighboring molecules. In the crystal of **III**, one of the amino H atoms forms an intramolecular  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bond; adjacent molecules are linked by  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds, forming a chain running along  $[10\bar{2}]$ . In the crystal of **IV**, intermolecular  $\text{N}-\text{H}\cdots\text{N}$ ,  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{N}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules into a three-dimensional network.

#### 5. Synthesis and crystallization

Equimolar amounts of (*Z*)-3-bromo-4-ethoxy-1,1,1-trifluorobut-3-en-2-one (0.247 g, 1.0 mmol) and diaminofurazan (0.100 g, 1.0 mmol) were dissolved in 25 ml of ethanol and refluxed for 3 h. The reaction was monitored by  $^1\text{H}$  NMR. A characteristic disappearance of the signals associated with the ethoxy group was observed. At the end of the reaction, the solvent was removed *in vacuo*. (3*Z*)-4-[(4-amino-1,2,5-oxadiazol-3-yl)amino]-3-bromo-1,1,1-trifluorobut-3-en-2-one in the form of a yellow precipitate, which was then recrystallized from acetone. Yield 0.249 g (83%); m.p. 444–445 K. Analysis calculated (%) for  $\text{C}_6\text{H}_4\text{BrF}_3\text{N}_4\text{O}_2$ : C 23.94, H 1.34, Br 26.54, F 18.93, N 18.93, O 10.63; found: C 23.92, H 1.31, Br 26.57, F 18.93, N 18.94, O 10.60.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ ): 5.88 (*br*, 2H,  $\text{NH}_2$ ), 8.52 (*s*, 1H, CH), 9.05 (*br*, 1H, NH).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ): 97.89, 114.30, 120.06, 146.71, 147.01, 206.20. ESI-MS:  $m/z$ : 298.9408 [ $M - \text{H}$ ] $^+$ .



**Table 2**

Experimental details.

Crystal data	
Chemical formula	C <sub>6</sub> H <sub>4</sub> BrF <sub>3</sub> N <sub>4</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	301.04
Crystal system, space group	Monoclinic, <i>P2<sub>1</sub>/n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.95281 (3), 14.0515 (1), 13.5208 (1)
β (°)	95.1372 (6)
<i>V</i> (Å <sup>3</sup> )	937.19 (1)
<i>Z</i>	4
Radiation type	Cu Kα
μ (mm <sup>-1</sup> )	6.46
Crystal size (mm)	0.21 × 0.04 × 0.04
Data collection	
Diffraction	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian ( <i>CrysAlis PRO</i> ; Rigaku OD, 2023)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.490, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	24751, 2038, 2010
<i>R<sub>int</sub></i>	0.030
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.638
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.028, 0.065, 1.09
No. of reflections	2038
No. of parameters	159
No. of restraints	3
H-atom treatment	All H-atom parameters refined
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.73, -0.50

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in a difference map and freely refined. The F atoms of the trifluoromethyl group are disordered over two sites in a 0.515 (6): 0.485 (6) ratio. The C–F bond lengths in the disordered trifluoromethyl group were constrained to be the same (using SADI), as were the thermal parameters of the F atoms (using EADP).

## Acknowledgements

The authors' contributions are as follows. Conceptualization, FIG, MA and AB; synthesis, VOO, BIU, OML and AIS; X-ray analysis, VOO, BIU, OML and AIS; writing (review and editing of the manuscript) FIG, STÇ and MA; supervision, MA and AB.

## References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Chandra, G., Singh, D. V., Mahato, G. K. & Patel, S. (2023). *Chem. Pap.* **77**, 4085–4106.  
 Chang, J., Hu, L., Pang, S. & He, C. (2023). *J. Mater. Chem. A*, **11**, 15979–15985.

Chen, W., Chen, C., Chang, T. T., Hsieh, F. C., Chen, W. & Li, W. (2022). *J. Chin. Chem. Soc.* **69**, 375–387.  
 Dutta, S., Liu, N., Gao, Y., Beck, L. & Wang, X. (2022). *Bioorg. Med. Chem. Lett.* **72**, 128878.  
 Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.  
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.  
 Gurbanov, A. V., Kuznetsov, M. L., Karmakar, A., Aliyeva, V. A., Mahmudov, K. T. & Pombeiro, A. J. L. (2022a). *Dalton Trans.* **51**, 1019–1031.  
 Gurbanov, A. V., Kuznetsov, M. L., Mahmudov, K. T., Pombeiro, A. J. L. & Resnati, G. (2020). *Chem. A Eur. J.* **26**, 14833–14837.  
 Gurbanov, A. V., Kuznetsov, M. L., Resnati, G., Mahmudov, K. T. & Pombeiro, A. J. L. (2022b). *Cryst. Growth Des.* **22**, 3932–3940.  
 Han, J. L., Remete, A. M., Dobson, L. S., Kiss, L., Izawa, K., Moriwaki, H., Soloshonok, V. A. & O'Hagan, D. (2020). *J. Fluor. Chem.* **239**, 109639.  
 Jia, S.-Y., Wang, B.-Z., Fan, X.-Z., Li, P. & Ng, S. W. (2012). *Acta Cryst.* **E68**, o1573.  
 Kopylovich, M. N., Gajewska, M. J., Mahmudov, K. T., Kirillova, M. V., Figiel, P. J., Guedes da Silva, M. F. C., Gil-Hernández, B., Sanchiz, J. & Pombeiro, A. J. L. (2012). *New J. Chem.* **36**, 1646–1654.  
 Kopylovich, M. N., Karabach, Y. Y., Mahmudov, K. T., Haukka, M., Kirillov, A. M., Figiel, P. J. & Pombeiro, A. J. L. (2011a). *Cryst. Growth Des.* **11**, 4247–4252.  
 Kopylovich, M. N., Mahmudov, K. T., Haukka, M., Luzyanin, K. V. & Pombeiro, A. J. L. (2011b). *Inorg. Chim. Acta*, **374**, 175–180.  
 Liao, S., Deng, M. & Song, S. (2020). *Chin. J. Energetic Mater.* **28**, 632–637.  
 Liu, Y., Zeng, Z., Huang, W., Shreeve, J. M. & Tang, Y. (2022). *J. Org. Chem.* **87**, 4226–4231.  
 Mac Leod, T. C., Kopylovich, M. N., Guedes da Silva, M. F. C., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *Appl. Catal. Gen.* **439–440**, 15–23.  
 Mahmudov, K. T., Kopylovich, M. N., Haukka, M., Mahmudova, G. S., Esmaeila, E. F., Chyragov, F. M. & Pombeiro, A. J. L. (2013). *J. Mol. Struct.* **1048**, 108–112.  
 Martins, N. M. R., Anbu, S., Mahmudov, K. T., Ravishankaran, R., Guedes da Silva, M. F. C., Martins, L. M. D. R. S., Karande, A. A. & Pombeiro, A. J. L. (2017). *New J. Chem.* **41**, 4076–4086.  
 Meanwell, N. A. (2018). *J. Med. Chem.* **61**, 5822–5880.  
 Mei, H., Han, J., Fustero, S., Medjo-Simon, M., Sedgwick, D. M., Santi, C., Ruzziconi, R. & Soloshonok, V. A. (2019). *Chem. A Eur. J.* **25**, 11797–11819.  
 Mizar, A., Guedes da Silva, M. F. C., Kopylovich, M. N., Mukherjee, S., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *Eur. J. Inorg. Chem.* pp. 2305–2313.  
 Okmanov, R. Y., Ziyayev, A. A., Abdugarimov, A. S., Toshmurodov, T. T. & Kholikov, T. S. (2023). *Acta Cryst.* **E79**, 552–556.  
 Rigaku OD (2023). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.  
 Shabir, G., Saeed, A., Zahid, W., Naseer, F., Riaz, Z., Khalil, N., Muneeba & Albericio, F. (2023). *Pharmaceuticals*, **16**, 1162.  
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.  
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.  
 Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.  
 Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.  
 Ugrak, B. I., Shkineva, T. K., Sheremetev, A. B. & Dalinger, I. L. (2023). *Russ. Chem. Bull.* **72**, 2706–2716.  
 Zhang, C., Yan, K., Fu, C., Peng, H., Hawker, C. J. & Whittaker, A. K. (2022). *Chem. Rev.* **122**, 167–208.  
 Zhang, H. & Jian, F. (2009). *Acta Cryst.* **E65**, o2911.

## supporting information

*Acta Cryst.* (2024). E80 [https://doi.org/10.1107/S2056989024004080]

## Synthesis, crystal structure and Hirshfeld surface analysis of (3Z)-4-[(4-amino-1,2,5-oxadiazol-3-yl)amino]-3-bromo-1,1,1-trifluorobut-3-en-2-one

**Firudin I. Guseinov, Sevim Türktekin Çelikesir, Mehmet Akkurt, Viacheslav O. Ovsyannikov, Bogdan I. Ugrak, Oksana M. Lavrova, Aida I. Samigullina and Ajaya Bhattarai**

### Computing details

(3Z)-4-[(4-Amino-1,2,5-oxadiazol-3-yl)amino]-3-bromo-1,1,1-trifluorobut-3-en-2-one

#### Crystal data

$C_6H_4BrF_3N_4O_2$	$F(000) = 584$
$M_r = 301.04$	$D_x = 2.134 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 4.95281 (3) \text{ \AA}$	Cell parameters from 17512 reflections
$b = 14.0515 (1) \text{ \AA}$	$\theta = 4.5\text{--}78.8^\circ$
$c = 13.5208 (1) \text{ \AA}$	$\mu = 6.46 \text{ mm}^{-1}$
$\beta = 95.1372 (6)^\circ$	$T = 100 \text{ K}$
$V = 937.19 (1) \text{ \AA}^3$	Block, colorless
$Z = 4$	$0.21 \times 0.04 \times 0.04 \text{ mm}$

#### Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	$T_{\min} = 0.490$ , $T_{\max} = 1.000$
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	24751 measured reflections
Mirror monochromator	2038 independent reflections
Detector resolution: $10.0000 \text{ pixels mm}^{-1}$	2010 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.030$
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2023)	$\theta_{\max} = 79.7^\circ$ , $\theta_{\min} = 4.6^\circ$
	$h = -5 \rightarrow 6$
	$k = -17 \rightarrow 17$
	$l = -17 \rightarrow 17$

#### Refinement

Refinement on $F^2$	Hydrogen site location: difference Fourier map
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 2.0497P]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\max} < 0.001$
2038 reflections	$\Delta\rho_{\max} = 0.73 \text{ e \AA}^{-3}$
159 parameters	$\Delta\rho_{\min} = -0.50 \text{ e \AA}^{-3}$
3 restraints	

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br9	0.19184 (5)	0.35928 (2)	0.19637 (2)	0.02267 (9)	
F12	0.8845 (8)	0.5446 (3)	0.3711 (3)	0.0259 (3)	0.515 (6)
F13	0.5295 (8)	0.5812 (3)	0.4473 (3)	0.0259 (3)	0.515 (6)
F14	0.6521 (9)	0.6697 (4)	0.3275 (4)	0.0259 (3)	0.515 (6)
F12A	0.8549 (8)	0.5453 (3)	0.4018 (3)	0.0259 (3)	0.485 (6)
F14A	0.7062 (9)	0.6639 (4)	0.3163 (4)	0.0259 (3)	0.485 (6)
F13A	0.4825 (8)	0.6121 (3)	0.4364 (3)	0.0259 (3)	0.485 (6)
O2	1.2074 (4)	0.20748 (12)	0.50222 (14)	0.0254 (4)	
O10	0.2781 (4)	0.57289 (12)	0.23355 (13)	0.0249 (4)	
N1	1.0965 (4)	0.11662 (14)	0.48774 (16)	0.0220 (4)	
N3	1.0442 (4)	0.27473 (15)	0.45145 (17)	0.0254 (4)	
N6	0.7135 (5)	0.05515 (16)	0.3947 (2)	0.0298 (5)	
H6A	0.568 (7)	0.065 (2)	0.373 (3)	0.029 (9)*	
H6B	0.748 (7)	0.000 (3)	0.427 (3)	0.033 (9)*	
N7	0.6329 (4)	0.27298 (14)	0.35067 (15)	0.0194 (4)	
H7	0.525 (6)	0.241 (2)	0.316 (2)	0.024 (8)*	
C4	0.8417 (5)	0.22775 (16)	0.40856 (17)	0.0195 (4)	
C5	0.8708 (5)	0.12796 (17)	0.43003 (18)	0.0197 (4)	
C8	0.6209 (5)	0.36888 (17)	0.34691 (18)	0.0198 (5)	
H8	0.748 (6)	0.400 (2)	0.393 (2)	0.019 (7)*	
C9	0.4468 (5)	0.42186 (16)	0.28686 (17)	0.0192 (4)	
C10	0.4376 (5)	0.52457 (17)	0.28565 (17)	0.0199 (5)	
C11	0.6293 (5)	0.58284 (17)	0.36048 (18)	0.0224 (5)	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br9	0.02440 (14)	0.01774 (14)	0.02471 (14)	−0.00003 (9)	−0.00423 (9)	−0.00055 (9)
F12	0.0292 (8)	0.0196 (6)	0.0282 (7)	−0.0003 (6)	−0.0016 (6)	−0.0005 (7)
F13	0.0292 (8)	0.0196 (6)	0.0282 (7)	−0.0003 (6)	−0.0016 (6)	−0.0005 (7)
F14	0.0292 (8)	0.0196 (6)	0.0282 (7)	−0.0003 (6)	−0.0016 (6)	−0.0005 (7)
F12A	0.0292 (8)	0.0196 (6)	0.0282 (7)	−0.0003 (6)	−0.0016 (6)	−0.0005 (7)
F14A	0.0292 (8)	0.0196 (6)	0.0282 (7)	−0.0003 (6)	−0.0016 (6)	−0.0005 (7)
F13A	0.0292 (8)	0.0196 (6)	0.0282 (7)	−0.0003 (6)	−0.0016 (6)	−0.0005 (7)
O2	0.0264 (9)	0.0158 (8)	0.0317 (9)	−0.0015 (7)	−0.0105 (7)	0.0016 (7)
O10	0.0278 (9)	0.0194 (8)	0.0261 (9)	0.0031 (7)	−0.0062 (7)	0.0032 (7)
N1	0.0236 (10)	0.0156 (9)	0.0258 (10)	0.0000 (8)	−0.0031 (8)	0.0003 (8)
N3	0.0263 (10)	0.0171 (10)	0.0308 (11)	0.0009 (8)	−0.0090 (9)	0.0023 (8)
N6	0.0219 (11)	0.0165 (10)	0.0478 (14)	−0.0013 (8)	−0.0142 (10)	0.0046 (10)

N7	0.0190 (9)	0.0147 (9)	0.0238 (10)	0.0004 (8)	-0.0024 (8)	0.0006 (8)
C4	0.0198 (11)	0.0166 (11)	0.0216 (11)	0.0012 (8)	-0.0009 (8)	0.0009 (9)
C5	0.0194 (10)	0.0174 (11)	0.0218 (11)	0.0019 (8)	-0.0005 (9)	0.0015 (9)
C8	0.0216 (11)	0.0166 (11)	0.0210 (11)	0.0009 (9)	0.0008 (9)	-0.0009 (9)
C9	0.0204 (11)	0.0166 (11)	0.0202 (11)	-0.0018 (9)	-0.0002 (8)	-0.0007 (8)
C10	0.0209 (11)	0.0179 (11)	0.0209 (11)	-0.0004 (9)	0.0006 (8)	0.0015 (9)
C11	0.0256 (12)	0.0180 (11)	0.0227 (11)	-0.0004 (9)	-0.0026 (9)	0.0029 (9)

*Geometric parameters (Å, °)*

Br9—C9	1.894 (2)	N6—C5	1.347 (3)
F12—C11	1.369 (5)	N6—H6A	0.76 (4)
F13—C11	1.314 (4)	N6—H6B	0.89 (4)
F14—C11	1.307 (5)	N7—C8	1.350 (3)
F12A—C11	1.314 (5)	N7—C4	1.393 (3)
F14A—C11	1.356 (6)	N7—H7	0.82 (3)
F13A—C11	1.373 (5)	C4—C5	1.437 (3)
O2—N3	1.385 (3)	C8—C9	1.353 (3)
O2—N1	1.397 (3)	C8—H8	0.95 (3)
O10—C10	1.217 (3)	C9—C10	1.444 (3)
N1—C5	1.314 (3)	C10—C11	1.557 (3)
N3—C4	1.294 (3)		
N3—O2—N1	110.46 (17)	C8—C9—C10	125.1 (2)
C5—N1—O2	105.97 (18)	C8—C9—Br9	118.96 (18)
C4—N3—O2	105.58 (19)	C10—C9—Br9	115.99 (17)
C5—N6—H6A	120 (3)	O10—C10—C9	125.6 (2)
C5—N6—H6B	114 (2)	O10—C10—C11	114.1 (2)
H6A—N6—H6B	118 (3)	C9—C10—C11	120.1 (2)
C8—N7—C4	120.3 (2)	F14—C11—F13	111.9 (3)
C8—N7—H7	120 (2)	F12A—C11—F14A	105.3 (3)
C4—N7—H7	119 (2)	F14—C11—F12	107.1 (3)
N3—C4—N7	121.7 (2)	F13—C11—F12	108.5 (3)
N3—C4—C5	110.3 (2)	F12A—C11—F13A	106.8 (3)
N7—C4—C5	127.9 (2)	F14A—C11—F13A	105.4 (3)
N1—C5—N6	123.5 (2)	F14—C11—C10	109.6 (3)
N1—C5—C4	107.6 (2)	F13—C11—C10	108.3 (2)
N6—C5—C4	128.7 (2)	F12A—C11—C10	120.7 (3)
N7—C8—C9	126.5 (2)	F14A—C11—C10	109.5 (3)
N7—C8—H8	114.1 (18)	F12—C11—C10	111.4 (3)
C9—C8—H8	119.4 (18)	F13A—C11—C10	108.1 (2)
N3—O2—N1—C5	-0.3 (3)	Br9—C9—C10—O10	1.6 (3)
N1—O2—N3—C4	0.5 (3)	C8—C9—C10—C11	-2.8 (4)
O2—N3—C4—N7	179.6 (2)	Br9—C9—C10—C11	177.15 (17)
O2—N3—C4—C5	-0.5 (3)	O10—C10—C11—F14	-24.2 (4)
C8—N7—C4—N3	-7.5 (4)	C9—C10—C11—F14	159.8 (3)
C8—N7—C4—C5	172.6 (2)	O10—C10—C11—F13	98.1 (3)

O2—N1—C5—N6	176.1 (2)	C9—C10—C11—F13	-77.9 (3)
O2—N1—C5—C4	0.0 (3)	O10—C10—C11—F12A	-161.5 (3)
N3—C4—C5—N1	0.4 (3)	C9—C10—C11—F12A	22.5 (4)
N7—C4—C5—N1	-179.7 (2)	O10—C10—C11—F14A	-39.1 (4)
N3—C4—C5—N6	-175.5 (3)	C9—C10—C11—F14A	144.9 (3)
N7—C4—C5—N6	4.4 (4)	O10—C10—C11—F12	-142.7 (3)
C4—N7—C8—C9	173.0 (2)	C9—C10—C11—F12	41.4 (3)
N7—C8—C9—C10	179.2 (2)	O10—C10—C11—F13A	75.2 (3)
N7—C8—C9—Br9	-0.7 (4)	C9—C10—C11—F13A	-100.8 (3)
C8—C9—C10—O10	-178.3 (2)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N6—H6 <i>A</i> ...O10 <sup>i</sup>	0.77 (4)	2.14 (4)	2.871 (3)	159 (4)
N6—H6 <i>B</i> ...N1 <sup>ii</sup>	0.90 (4)	2.11 (4)	2.995 (3)	169 (3)
N7—H7...Br9	0.81 (3)	2.76 (3)	3.127 (2)	109 (2)
C8—H8...F12	0.95 (3)	2.17 (3)	2.799 (5)	123 (2)
C8—H8...F12 <i>A</i>	0.95 (3)	2.11 (3)	2.808 (5)	129 (2)
C8—H8...N3	0.95 (3)	2.38 (3)	2.759 (3)	103.3 (19)

Symmetry codes: (i)  $-x+1/2, y-1/2, -z+1/2$ ; (ii)  $-x+2, -y, -z+1$ .