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Chalcogen bonds in the crystal structure of 4,7-dibromo-2,1,3-benzoselenadiazole, $C_6H_2Br_2N_2Se$

Figure 1: Molecular structure of the title compound with displacement ellipsoids draw at the 50% probability level.

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Abstract

$C_6H_2Br_2N_2Se$, monoclinic, $P2_1/c$ (no. 14), $a = 7.7277(4)$ Å, $b = 19.6360(6)$ Å, $c = 10.8656(5)$ Å, $\beta = 102.124(4)^\circ$, $V = 1611.98(12)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0482$, $wR_{ref}(F^2) = 0.1175$, $T = 290$ K.

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The asymmetric unit of the title crystal structure is shown in the Figure 1. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The 4,7-dibromo-2,1,3-benzoselenadiazole was purchased from Alfa Chemical Co. Ltd. (Zhengzhou, China) and used without further purification. The 4,7-dibromo-2,1,3-benzoselenadiazole (3.41 mg, 0.01 mmol) was dissolved in approximately 10 mL of methanol with gentle stirring at room temperature. Then, the solution was set aside for

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.32 × 0.28 × 0.17 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	14.5 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	28.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	18,469, 3636, 0.075
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2375
$N(param)_{refined}$:	199
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

crystallization by slow evaporation of the solvent at room temperature conditions. After about two days, brown block crystals of title compound suitable for single-crystal X-ray diffraction were obtained.

Experimental details

The structure was solved with the SHELXT [3] program using Intrinsic Phasing and refined with the SHELXL [4] refinement package. H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with $U_{iso}(H)$ set to $1.2U_{eq}(C)$.

Comment

The term chalcogen bond was coined in 2009 [5]. Ten years later, the International Union of Pure and Applied Chemistry (IUPAC) issued a formal definition of the chalcogen bond [6]. In the crystals involving 2,1,3-benzoselenadiazole or its derivatives, the four-membered $[Se-N]_2$ cyclic double chalcogen bonds were always formed [7]. Besides the cyclic double chalcogen bonds, the other types of chalcogen bonds can also be formed between the 2,1,3-benzoselenadiazole or its derivatives and their coformers [8]. In this work, we studied the non-covalent interactions in the crystal of 4,7-dibromo-2,1,3-benzoselenadiazole. The focus of attention is: what kind of chalcogen bond can be formed in the title crystal.

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.51340 (11)	0.82695 (4)	0.67016 (8)	0.0569 (2)
Br2	0.56356 (10)	0.50297 (4)	0.82913 (7)	0.0510 (2)
Se1	0.25275 (9)	0.61923 (3)	0.44783 (6)	0.0386 (2)
N1	0.3403 (7)	0.6984 (3)	0.5138 (5)	0.0380 (13)
N2	0.3542 (6)	0.5706 (3)	0.5841 (5)	0.0330 (12)
C1	0.4348 (8)	0.6850 (3)	0.6276 (6)	0.0301 (14)
C2	0.5266 (8)	0.7341 (3)	0.7143 (6)	0.0377 (16)
C3	0.6242 (8)	0.7143 (3)	0.8267 (6)	0.0418 (17)
H3	0.6848	0.7469	0.8815	0.050*
C4	0.6360 (9)	0.6440 (4)	0.8628 (6)	0.0437 (17)
H4	0.7041	0.6315	0.9406	0.052*
C5	0.5482 (8)	0.5952 (3)	0.7843 (6)	0.0338 (15)
C6	0.4431 (8)	0.6140 (3)	0.6654 (5)	0.0299 (14)
Br3	−0.01261 (10)	0.22100 (4)	0.31893 (8)	0.0592 (3)
Br4	−0.06430 (10)	0.54466 (4)	0.15761 (7)	0.0482 (2)
Se2	0.25383 (8)	0.42750 (4)	0.53765 (6)	0.0379 (2)
N3	0.1699 (7)	0.3480 (3)	0.4694 (5)	0.0367 (13)
N4	0.1468 (6)	0.4774 (2)	0.4045 (5)	0.0340 (12)
C7	0.0702 (8)	0.3615 (3)	0.3575 (6)	0.0306 (14)
C8	−0.0253 (8)	0.3134 (3)	0.2715 (6)	0.0399 (16)
C9	−0.1235 (9)	0.3331 (3)	0.1608 (6)	0.0410 (17)
H9	−0.1855	0.3008	0.1063	0.049*
C10	−0.1345 (8)	0.4035 (3)	0.1250 (6)	0.0377 (16)
H10	−0.2027	0.4159	0.0471	0.045*
C11	−0.0476 (8)	0.4523 (3)	0.2019 (6)	0.0322 (14)
C12	0.0582 (7)	0.4333 (3)	0.3212 (5)	0.0269 (13)

All bond lengths and angles in the title crystal structure are in the normal ranges. The 4,7-dibromo-2,1,3-benzoselenadiazole molecules form 2D corrugated sheets which further self-assemble into a 3D layered structure. There are five types of non-covalent interactions in the crystal structure: the four-membered $[\text{Se} \cdots \text{N}]_2$ cyclic double chalcogen bonds, $\text{N} \cdots \text{Se} \cdots \text{Br}$ chalcogen bonds, $\text{C} \cdots \text{H} \cdots \text{N}$ hydrogen bonds, $\pi \cdots \pi$ stacking interactions and σ -hole($\text{Br} \cdots \sigma$ -hole(Br) stacking interactions [9, 10]; among them, the four-membered $[\text{Se} \cdots \text{N}]_2$ cyclic double chalcogen bonds and $\pi \cdots \pi$ stacking interactions are much stronger. According to the dispersion-corrected density functional theory calculations at the PBE0-D3/def2-TZVPP level of theory [11, 12], the binding energy of the four-membered $[\text{Se} \cdots \text{N}]_2$ cyclic double chalcogen bonds between two 4,7-dibromo-2,1,3-benzoselenadiazole molecules is 10.27 kcal/mol, and the binding energy of the $\pi \cdots \pi$ stacking interactions between two 4,7-dibromo-2,1,3-benzoselenadiazole molecules is 8.55 kcal/mol. The details and reliability of the PBE0-D3/def2-TZVPP calculations for the study of the non-covalent interactions can be found elsewhere [13–15]. Evidently, the larger binding energy of the four-membered $[\text{Se} \cdots \text{N}]_2$ cyclic double chalcogen

bonds between two 4,7-dibromo-2,1,3-benzoselenadiazole molecules explains why the four-membered $[\text{Se} \cdots \text{N}]_2$ cyclic double chalcogen bonds were always found in the crystals involving 2,1,3-benzoselenadiazole or its derivatives.

In conclusion, there are two types of chalcogen bonds in the crystal of 4,7-dibromo-2,1,3-benzoselenadiazole. One type is of the much stronger four-membered $[\text{Se} \cdots \text{N}]_2$ cyclic double chalcogen bonds, and the other is of the much weaker $\text{N} \cdots \text{Se} \cdots \text{Br}$ chalcogen bonds.

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