Crystal structure of 4,7-dibromo-2,1,3-benzothiadiazole, $C_6H_2Br_2N_2S$

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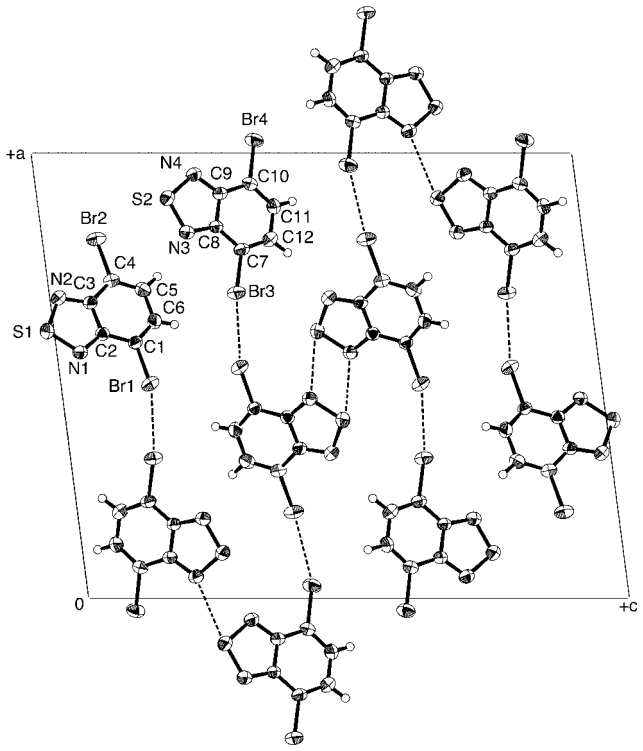

Abstract

$C_6H_2Br_2N_2S$, monoclinic, $P12_1/c1$ (No. 14), a = 18.3670(9) Å, b = 3.9522(2) Å, c = 22.120(2) Å, β = 97.390(6)°, V = 1592.4 Å^3, Z = 8, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.127, T = 296 K.

Source of material

The title compound was synthesized by bromination of 2,1,3-benzothiadiazole in 47% HBr [1]. Pale yellow crystals suitable for X-ray analysis were grown from a dichloromethane solution.

Discussion

The title compound crystallizes with two crystallographically independent molecules in the asymmetric unit. The geometric parameters of the 1,2,5-thiadiazole rings are almost same with those of 3,4-diphenyl-1,2,5-thiadiazole [2]. The considerable shortenings of the C1—C6, C4—C5, C7—C12 and C10—C11 bonds are observed. Such double bond fixation suggests the quinonoid character of the 2,1,3-benzothiadiazole ring. Short S···N and Br···Br intermolecular heteroatom contacts are found in the crystal. The S···N [3.226(4) Å for S1···N1 (–x+1, –y+1, –z) and 3.238(4) Å for S2···N4(–x+2, y+1/2, –z+1/2)] and the distances Br···Br [3.542(1) Å for Br1···Br3(–x+1, y–1/2, –z+1/2) and 3.662(1) Å for Br2···Br4(–x+2, y–1/2, –z+1/2)] are 3.4% – 3.7% and 1.0% – 4.3% shorter than the sum of the corresponding van der Waals radii [3], respectively. Although a planar I_4 square cluster via the short intermolecular I···I contacts was formed in the crystal of 4,7-diiodo-2,1,3-benzothiadiazole [4], no Br_4 square clusters exist in the structure of the title compound.

Table 1. Data collection and handling.

Crystal:	pale yellow plate, size 0.05 × 0.10 × 0.60 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	147.99 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	148.44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3313, 3219
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2772
$N(param)_{refined}$:	216
Programs:	TeXsan [5], SHELXS-97 [6], SHELXL-97 [7], ORTEP-III [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(5)	4*e*	0.722(4)	–0.36(2)	0.204(3)	0.10(2)
H(6)	4*e*	0.615(4)	–0.17(2)	0.224(3)	0.07(2)
H(11)	4*e*	0.891(4)	–0.26(1)	0.472(3)	0.07(2)
H(12)	4*e*	0.776(3)	–0.11(1)	0.451(2)	0.05(1)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4*e*	0.48143(3)	0.2025(1)	0.16536(2)	0.0381(3)	0.0519(3)	0.0558(3)	0.0025(2)	0.0192(2)	–0.0028(2)
Br(2)	4*e*	0.80623(3)	–0.2799(1)	0.10005(3)	0.0325(3)	0.0501(3)	0.0688(4)	0.0052(2)	0.0109(2)	–0.0010(2)
Br(3)	4*e*	0.68579(2)	0.2462(1)	0.34649(2)	0.0296(3)	0.0573(3)	0.0608(3)	0.0047(2)	0.0086(2)	0.0006(2)
Br(4)	4*e*	1.02795(3)	–0.2683(1)	0.41600(2)	0.0346(3)	0.0503(3)	0.0589(3)	0.0063(2)	–0.0018(2)	0.0085(2)
S(1)	4*e*	0.59971(7)	0.2962(3)	–0.01294(5)	0.0443(6)	0.0569(7)	0.0350(5)	–0.0024(5)	0.0059(4)	0.0071(4)
S(2)	4*e*	0.89837(7)	0.2796(3)	0.24129(5)	0.0392(6)	0.0702(8)	0.0395(5)	0.0021(5)	0.0095(4)	0.0112(5)
N(1)	4*e*	0.5520(2)	0.2898(9)	0.0432(2)	0.032(2)	0.044(2)	0.039(2)	0.001(1)	0.004(1)	0.004(1)
N(2)	4*e*	0.6740(2)	0.105(1)	0.0164(2)	0.039(2)	0.050(2)	0.041(2)	–0.002(2)	0.011(1)	0.002(2)
N(3)	4*e*	0.8215(2)	0.2891(9)	0.2691(2)	0.033(2)	0.051(2)	0.043(2)	0.000(1)	0.003(2)	0.004(2)
N(4)	4*e*	0.9512(2)	0.099(1)	0.2958(2)	0.033(2)	0.055(2)	0.043(2)	0.005(2)	0.009(1)	0.005(2)
C(1)	4*e*	0.5739(2)	0.058(1)	0.1479(2)	0.030(2)	0.037(2)	0.036(2)	–0.003(2)	0.008(1)	–0.003(2)
C(2)	4*e*	0.5936(2)	0.129(1)	0.0890(2)	0.031(2)	0.034(2)	0.035(2)	–0.003(2)	0.004(1)	0.001(2)
C(3)	4*e*	0.6637(2)	0.025(1)	0.0738(2)	0.029(2)	0.039(2)	0.037(2)	–0.004(2)	0.005(1)	–0.002(2)
C(4)	4*e*	0.7132(2)	–0.144(1)	0.1184(2)	0.031(2)	0.033(2)	0.047(2)	0.000(2)	0.008(2)	0.000(2)
C(5)	4*e*	0.6926(3)	–0.209(1)	0.1743(2)	0.038(2)	0.044(2)	0.044(2)	–0.001(2)	–0.001(2)	0.004(2)
C(6)	4*e*	0.6221(2)	–0.108(1)	0.1884(2)	0.043(2)	0.049(2)	0.033(2)	–0.006(2)	0.006(2)	0.002(2)
C(7)	4*e*	0.7830(2)	0.097(1)	0.3666(2)	0.028(2)	0.041(2)	0.044(2)	0.001(2)	0.008(2)	–0.003(2)
C(8)	4*e*	0.8340(2)	0.146(1)	0.3245(2)	0.026(2)	0.034(2)	0.036(2)	0.001(1)	0.004(1)	–0.002(2)
C(9)	4*e*	0.9086(2)	0.035(1)	0.3399(2)	0.028(2)	0.037(2)	0.038(2)	–0.000(1)	0.005(1)	–0.000(2)
C(10)	4*e*	0.9304(2)	–0.122(1)	0.3971(2)	0.030(2)	0.035(2)	0.041(2)	0.001(2)	0.000(1)	–0.000(2)
C(11)	4*e*	0.8797(3)	–0.166(1)	0.4359(2)	0.043(2)	0.054(3)	0.033(2)	–0.001(2)	0.002(2)	0.008(2)
C(12)	4*e*	0.8057(2)	–0.057(1)	0.4210(2)	0.040(2)	0.055(3)	0.045(2)	–0.003(2)	0.014(2)	0.002(2)

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