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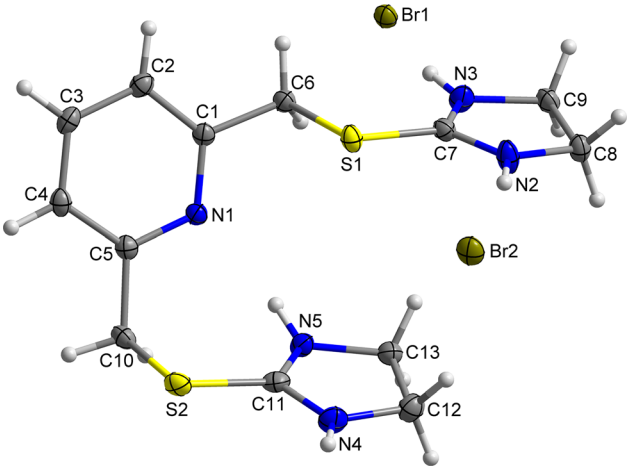
The crystal structure of 2,2′-((pyridine-2,6-diylbis(methylene))bis(sulfanediyl))-bis(4,5-dihydro-1*H*-imidazol-3-ium) bromide, $C_{13}H_{19}Br_2N_5S_2$



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Abstract

$C_{13}H_{19}Br_2N_5S_2$, triclinic, $P\bar{1}$ (no. 2), a = 5.22590(10) Å, b = 9.9960(2) Å, c = 17.0076(3) Å, α = 102.1340(15)°, β = 92.9160(16)°, γ = 90.7550(13)°, V = 867.21(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0205, $wR_{ref}(F^2)$ = 0.0737, T = 95 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.18 × 0.09 × 0.06 mm
Wavelength:	CuKα radiation (1.54184 Å)
μ:	8.21 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	73.1°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12478, 3406, 0.014
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3311
$N(param)_{refined}$:	211
Programs:	Rigaku [1], SUPERFLIP [2], JANA2006 [3], DIAMOND [4]

Source of material

The suspension of imidazoline-2-thione (0.435 g, 4.26 mmol) in acetonitrile (10 ml) was added to the solution of 2,6-bis(bromomethyl)pyridine (0.565 g, 2.13 mmol) in acetonitrile (10 ml). The reaction mixture was stirred for 8 h at room temperature. The resulting precipitate was filtered off, washed with acetonitrile (5 ml) and allowed to dry on air, resulting in yield of 0.915 g (91.5%). The single crystals for measurement were prepared by slow evaporation of acetonitrile solution of title compound (1 mg in 20 ml).

Experimental details

H atoms bonded at C were placed in calculated positions. H bonded to N were refined with restrained bond lengths (N—H = 0.86 Å). U_{iso}(H) = 1.2U_{eq}(C,N).

Comment

The title compound is a *N*,*N*′-substituted isothiouronium salt. The isothiouronium salts can act as $GABA_A$ agonists [5] and recently their antitumor activities have been described [6].

The asymmetric unit of the title compound crystal structure consists of one 2,2′-((pyridine-2,6-diylbis(methylene)) bis(sulfanediyl))bis(4,5-dihydro-1*H*-imidazol-3-ium) dication and two bromide anions, balancing the charges,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.33529 (4)	0.197076 (17)	0.099027 (10)	0.01685 (8)
Br2	1.01959 (4)	0.752068 (18)	0.492617 (11)	0.02181 (8)
S1	0.90807 (9)	0.55250 (4)	0.27126 (3)	0.01738 (13)
S2	0.91766 (9)	1.04456 (4)	0.23432 (3)	0.01912 (14)
N1	0.8634 (3)	0.71863 (14)	0.13947 (8)	0.0151 (4)
N2	0.6551 (3)	0.49229 (17)	0.39024 (9)	0.0234 (5)
N3	0.5189 (3)	0.36822 (16)	0.27336 (9)	0.0207 (5)
N4	0.6719 (3)	1.01812 (16)	0.36423 (10)	0.0230 (5)
N5	0.5492 (3)	0.86270 (15)	0.25689 (9)	0.0180 (4)
C1	0.9717 (3)	0.59553 (18)	0.12508 (10)	0.0152 (5)
C2	1.1844 (3)	0.56739 (18)	0.07925 (10)	0.0171 (5)
C3	1.2867 (4)	0.6717 (2)	0.04629 (11)	0.0176 (5)
C4	1.1777 (3)	0.79928 (18)	0.06116 (10)	0.0172 (5)
C5	0.9668 (3)	0.81921 (17)	0.10898 (10)	0.0151 (5)
C6	0.8508 (4)	0.48814 (18)	0.16298 (11)	0.0167 (5)
C7	0.6812 (4)	0.46424 (18)	0.31198 (11)	0.0162 (5)
C8	0.4400 (4)	0.41195 (18)	0.41111 (11)	0.0192 (5)
C9	0.3627 (4)	0.31634 (18)	0.33008 (11)	0.0193 (5)
C10	0.8420 (4)	0.95619 (17)	0.13000 (11)	0.0179 (5)
C11	0.7021 (3)	0.96934 (17)	0.28728 (11)	0.0173 (5)
C12	0.4821 (4)	0.9352 (2)	0.39584 (11)	0.0226 (6)
C13	0.4012 (4)	0.82400 (19)	0.32121 (11)	0.0196 (5)
H1n2	0.739 (4)	0.5587 (17)	0.4217 (12)	0.0281*
H1n3	0.513 (5)	0.329 (2)	0.2232 (4)	0.0249*
H1n4	0.762 (4)	1.0831 (18)	0.3947 (12)	0.0276*
H1n5	0.592 (5)	0.8053 (18)	0.2147 (8)	0.0216*
H1c2	1.259173	0.478622	0.070474	0.0206*
H1c3	1.431914	0.65493	0.013508	0.0212*
H1c4	1.245518	0.87232	0.039086	0.0206*
H1c6	0.936575	0.403167	0.147039	0.0201*
H2c6	0.669659	0.482152	0.149679	0.0201*
H1c8	0.301445	0.471526	0.427901	0.023*
H2c8	0.500871	0.358687	0.44876	0.023*
H1c9	0.410827	0.224606	0.331804	0.0232*
H2c9	0.184579	0.327135	0.316695	0.0232*
H1c10	0.659567	0.944034	0.120857	0.0215*
H2c10	0.895096	1.012692	0.094313	0.0215*
H1c12	0.3374	0.9901	0.412734	0.0271*
H2c12	0.564654	0.89361	0.436051	0.0271*
H1c13	0.454976	0.736424	0.329701	0.0235*
H2c13	0.221232	0.830057	0.30845	0.0235*

see the figure. Both substituted isothiouronium groups are located on the same side of pyridine core. Viewing along the C6—S1 bond shows that the C1 and C7 atoms are close to the *anti-periplanar* conformation with the torsion angle C1—C6—S1—C7 at 159.90(13)°, while along the C10—S2 bond the conformation appears to be close to gauche with the C5—C10—S2—C11 torsion angle at −81.84(14)°. In both isothiouronium groups they are almost parallel with mean planes through the thiourea atoms forming an angle of 8.30(9)°. There is a significant difference between the C(Ar)—C(me)—S angles in both groups, with C1—C6—S1 angle at 104.58(11)°, while C5—C10—S2 angle is observed at 112.64(13)°. We attribute this difference to the hydrogen bonding and steric demands of the overall structure.

There are four strong hydrogen bonds in the structure with each isothiouronium nitrogen forming one hydrogen bond. The N2, N3, and N4 atoms form intermolecular N—H···Br bonds, while N5 forms an intramolecular N—H···N bond with the pyridine nitrogen,

causing the observed gauche conformation. The N—H···Br bonds involving Br2 connect two cations and two bromide anions into an $R_4^2(28)$ ring. Two N3—H1n3···Br1 bonds connect two Br1 anions to the ring, forming a neutral supramolecular block. The blocks are connected by numerous weak C—H···Br hydrogen bonds as well as C—H···S hydrogen bonds.

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

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