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Benzo-1,3,2-dithiazolium Iodide

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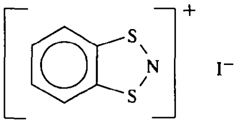
Abstract

The molecular structure of the iodide salt of the benzo-1,3,2-dithiazole cation, $C_6H_4NS_2^+.I^-$, has been determined. The cation was found to be planar to within 0.04 Å. The C_2S_2N ring is slightly asymmetrical, with S—N bonds of 1.584 (5) and 1.617 (6) Å. There is also significant localization of bonds within the benzene moiety. The ions are found to stack approximately parallel to the x axis. Alternating stacks are related by a 2_1 screw axis.

Comment

This study builds on our interest in the structures and transport properties of the charge-transfer salts of neutral heterocyclic thiazyl radicals (Bryan, Cordes, Haddon, Hicks, Kennepohl *et al.*, 1994; Bryan, Cordes, Haddon, Hicks, Oakley *et al.*, 1994; Bryan *et al.*, 1993). The title compound, (I), was prepared by oxidation of the neutral benzo-1,3,2-dithiazolyl radical (Awere *et al.*, 1990) with iodine in acetonitrile. Crystals of the salt suitable for X-ray study were grown by slow evaporation of the solvent.



(I)

The structure of the benzo-1,3,2-dithiazolium cation is shown in Fig. 1. The mean values for the chemically equivalent molecular parameters are similar to those found in the related chloride salt (Awere *et al.*, 1990), but the structure is less symmetrical. The two S—N distances are 1.584 (5) and 1.617 (6) Å. The C—C bond distances indicate significant localization of the bonding within the ring, as observed in the chloride salt. The closest I···S contact, 3.275 (1) Å, is between I and S(1)($x - \frac{1}{2}$, $\frac{3}{2} - y$, $1 - z$). The internal bond lengths of the heterocyclic ring, which are shorter than those found in the radical dimer (Awere *et al.*, 1990), coupled with the observation of discrete well separated iodide ions [I···I($\frac{1}{2} + x$, $\frac{3}{2} - y$, $2 - z$) 4.959 (2) Å], indicates a fully oxidized cation. This is in contrast to the structure of 4-phenyl-1,2,3,5-dithiadiazolium iodide, $PhCN_2S_2I$, which exists in the solid state as an intermediate oxidation state system $[PhCN_2S_2]_3[I_3]$ (Bryan *et al.*, 1993).

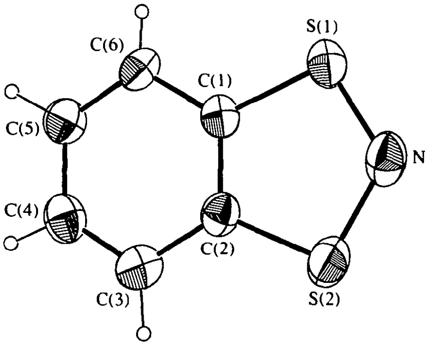


Fig. 1. *ORTEP*II plot (Johnson, 1976) of the title cation. Displacement ellipsoids are drawn at the 50% probability level.

In contrast to the chloride salt, the crystal structure of the iodide salt consists of slipped stacks of $H_4C_6S_2N$ rings and chains of iodide ions running parallel to the x axis (Fig. 2). Alternating stacks are related by a 2_1 screw axis. The perpendicular mean plane to mean plane separation of the herringbone-like arrays along the molecular stacks is 3.43 (2) Å.

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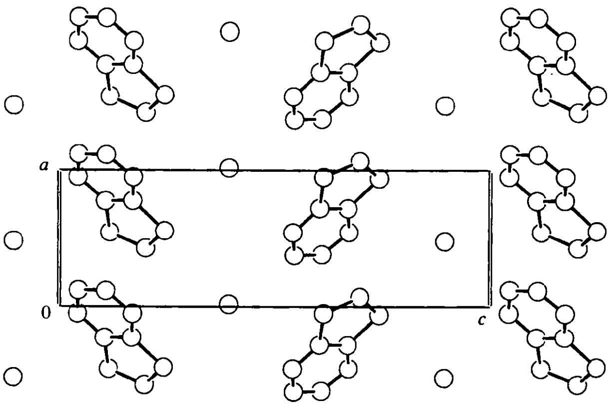

Fig. 2. The slipped stack arrangement of the cations and iodide chains running parallel to the x axis.

Experimental

Crystal data

$C_6H_4NS_2^+.I^-$
$M_r = 281.14$
Orthorhombic
$P2_12_12_1$
$a = 5.210 (2)$ Å
$b = 9.527 (3)$ Å
$c = 16.524 (6)$ Å
$V = 820.2$ Å^3
$Z = 4$
$D_x = 2.28$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11\text{–}15°$
$\mu = 4.27$ mm^{-1}
$T = 295$ K
Rectangular plate
0.30 × 0.10 × 0.08 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.789$, $T_{\max} = 0.999$
1142 measured reflections
1121 independent reflections

933 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 27.5°$
$h = -6 \rightarrow 0$
$k = -12 \rightarrow 0$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity decay: 11.8%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.030$
$S = 1.159$
933 reflections
104 parameters
Only coordinates of H atoms refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.03$

$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: *MolEN* (Fair, 1990)
Extinction coefficient: 5.9 (3) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\text{eq}} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
I	0.48031 (8)	0.87065 (4)	0.89291 (2)	3.276 (7)
S(1)	0.5478 (3)	0.8785 (2)	0.1133 (1)	3.16 (3)
S(2)	0.5575 (3)	1.0599 (2)	0.2421 (1)	3.99 (4)
N	0.430 (1)	0.9261 (6)	0.1973 (3)	3.7 (1)
C(1)	0.776 (1)	1.0084 (6)	0.1035 (4)	2.4 (1)
C(2)	0.778 (1)	1.1007 (7)	0.1683 (4)	2.7 (1)
C(3)	0.951 (1)	1.2139 (7)	0.1702 (4)	3.4 (1)
C(4)	1.116 (1)	1.2282 (7)	0.1070 (4)	3.4 (1)
C(5)	1.121 (1)	1.1310 (7)	0.0431 (4)	3.1 (1)
C(6)	0.954 (1)	1.0218 (6)	0.0407 (4)	2.9 (1)

Table 2. *Selected geometric parameters* (Å, °)

S(1)—N	1.584 (5)	C(2)—C(3)	1.404 (9)
S(2)—N	1.617 (6)	C(3)—C(4)	1.362 (9)
S(1)—C(1)	1.722 (6)	C(4)—C(5)	1.405 (9)
S(2)—C(2)	1.720 (6)	C(5)—C(6)	1.358 (9)
C(1)—C(2)	1.386 (9)	C(6)—C(1)	1.399 (8)
S(1)—N—S(2)	117.8 (3)	C(1)—C(2)—C(3)	120.7 (5)
N—S(1)—C(1)	98.3 (3)	C(2)—C(3)—C(4)	117.7 (6)
N—S(2)—C(2)	97.4 (3)	C(3)—C(4)—C(5)	121.5 (6)
S(1)—C(1)—C(2)	112.9 (5)	C(4)—C(5)—C(6)	121.0 (6)
S(2)—C(2)—C(1)	113.4 (4)	C(5)—C(6)—C(1)	118.3 (6)
S(1)—C(1)—C(6)	126.4 (5)	C(6)—C(1)—C(2)	120.6 (5)
S(2)—C(2)—C(3)	125.9 (5)		

*MULTAN*80 (Main *et al.*, 1980) was used to solve the structure. Other crystallographic calculations were performed using the *MolEN* package (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: CR1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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