

|             |             |              |            |
|-------------|-------------|--------------|------------|
| O32—P—O33   | 112.77 (12) | O2—C2—C1     | 109.3 (2)  |
| O31—P—O3    | 101.53 (11) | C3—C2—C1     | 112.3 (2)  |
| O32—P—O3    | 107.37 (12) | O1—C1—O11    | 125.2 (3)  |
| O33—P—O3    | 108.07 (12) | O1—C1—C2     | 118.6 (3)  |
| C3—O3—P     | 117.6 (2)   | O11—C1—C2    | 116.2 (3)  |
| C3—O3—P—O31 | 178.0 (2)   | O1—C1—C2—O2  | -23.5 (4)  |
| C3—O3—P—O32 | -61.7 (2)   | O11—C1—C2—O2 | 159.9 (2)  |
| C3—O3—P—O33 | 60.2 (2)    | O1—C1—C2—C3  | -147.3 (3) |
| P—O3—C3—C2  | -166.7 (2)  | O11—C1—C2—C3 | 36.1 (3)   |
| O2—C2—C3—O3 | 65.8 (3)    | C1—C2—C3—O3  | -171.4 (2) |

Table 4. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II)

| D—H...A                      | D—H      | H...A    | D...A     | D—H...A |
|------------------------------|----------|----------|-----------|---------|
| O2—H20...O1 <sup>i</sup>     | 0.79 (5) | 1.96 (5) | 2.728 (4) | 164 (4) |
| N1—H11N...O32                | 0.88 (4) | 1.78 (4) | 2.651 (4) | 171 (4) |
| N1—H12N...O11 <sup>ii</sup>  | 0.90 (4) | 2.03 (4) | 2.915 (4) | 169 (3) |
| N1—H13N...O33 <sup>iii</sup> | 0.79 (5) | 2.17 (6) | 2.817 (4) | 140 (5) |
| N1—H13N...O31 <sup>iii</sup> | 0.79 (5) | 2.47 (5) | 3.190 (4) | 151 (5) |
| N2—H21N...O31 <sup>iii</sup> | 0.84 (5) | 1.91 (5) | 2.745 (4) | 171 (4) |
| N2—H22N...O33                | 0.85 (5) | 1.90 (5) | 2.722 (4) | 163 (5) |
| N2—H23N...O4 <sup>iv</sup>   | 0.87 (4) | 2.20 (4) | 2.933 (4) | 142 (4) |
| N3—H31N...O1 <sup>i</sup>    | 0.87 (4) | 1.95 (4) | 2.785 (4) | 161 (4) |
| N3—H32N...O11 <sup>iv</sup>  | 0.88 (4) | 1.95 (4) | 2.801 (4) | 164 (4) |
| N3—H33N...O31                | 0.93 (4) | 1.86 (4) | 2.754 (4) | 162 (4) |
| N3—H33N...O3                 | 0.93 (4) | 2.55 (4) | 3.247 (4) | 133 (3) |
| O4—H4...O32                  | 0.89 (5) | 1.81 (5) | 2.691 (4) | 169 (4) |

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

For both crystals, the space group and approximate unit-cell parameters were determined from oscillation and Weissenberg photographs. A crystal of (I) was mounted on the diffractometer and cooled slowly to 150 K. After refinement, an additional significant peak was found on a difference map near one of the hydroxy groups of one of the [tris(hydroxymethyl)methyl]ammonium cations. It was admitted as a partially disordered  $-\text{CH}_2\text{OH}$  group. The structure of (II) was initially measured at 293 K and solved by direct methods. The displacement parameters for some of the C atoms of the cyclohexylammonium rings showed large values, suggesting disorder. Therefore, a second data set of reflections was collected at 85 K. Based on the new data set, the structure was refined again. In the case of (II), the standard reflections decreased in intensity by approximately 10% over the period of data collection; the data were therefore rescaled using the intensities of the standards. For both compounds, the absolute configuration was based on the known stereochemistry at C2. The C-bound H atoms were included in geometrically calculated positions for both compounds and the remaining H atoms were found from difference maps and refined isotropically. The crystal data for (II) at 293 (2) K are:  $a = 11.695$  (7),  $b = 9.197$  (8),  $c = 14.034$  (9)  $\text{\AA}$ ,  $\beta = 99.13$  (5) $^\circ$ ,  $V = 1490.4$  (3)  $\text{\AA}^3$  and  $D_x = 1.180$  (2)  $\text{Mg m}^{-3}$ .

For both compounds, data collection: *Kuma KM-4 User's Guide* (Kuma Diffraction, 1989); cell refinement: *Kuma KM-4 User's Guide*; data reduction: *Kuma KM-4 User's Guide*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1281). Services for accessing these data are described at the back of the journal.

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## S-Benzylisothiuronium Chloride

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### Abstract

The C—N bonds in  $\text{C}_8\text{H}_{11}\text{N}_2\text{S}^+\text{Cl}^-$ , a potent inhibitor of human nitric oxide synthase (HNOS), were found to be similar in length, indicating delocalization over the N—C—N fragment. The delocalization extends to the central C—S bond, indicating a structure more similar to a guanidine system than an amidinium one.

### Comment

Structural studies of amidines and amidinium salts continue to attract attention (Barker *et al.*, 1997; Barker & Kilner, 1994; Edelmann, 1994; Dehnicke, 1990) because of their catalytic, pharmaceutical and biological importance, and their coordination chemistry. The study of the title compound, (I), was carried out to furnish

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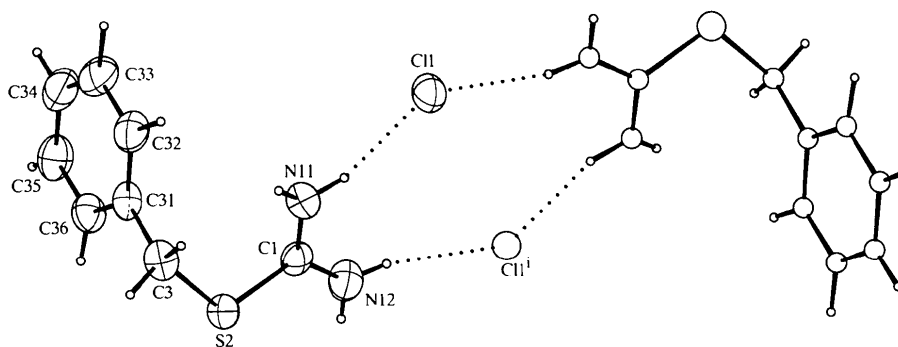


Fig. 1. The virtual dimer of the title compound; one moiety is represented as 50% probability displacement ellipsoids and the other as balls and sticks. [Symmetry code: (i)  $1 - x, -y, 1 - z$ .]

data on the effect of a heteroatom substituent on the central C atom of the amidine fragment, and to provide structural data on *S*-benzylisothiurea, which is a potent competitive inhibitor of human nitric oxide synthase (HNOS; Shearer *et al.*, 1997; Garvey *et al.*, 1994), itself a molecule of intense interest. There has been considerable research into the role of NO in biological systems in the past decade, which was brought to wider attention by its being named 'Molecule of the Year' in the journal *Science* (Koshland, 1992). Although there have been many reports on the biochemistry and biological activity of HNOS, its crystal structure has not yet been reported.

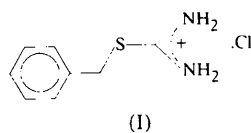


Fig. 2. Packing diagram viewed down the *a* axis showing the layers of hydrogen bonding.

The two C—N bond lengths in the title compound are similar [C1—N11 1.306 (4) and C1—N12 1.308 (4) Å] and are only slightly longer than the mean of 277  $C_{sp^2}=N$  double bonds [1.295 (12) Å] located in the Cambridge Structural Database (CSD; Allen *et al.*, 1987), indicating delocalization around the N—C—N fragment. The N11—C1—N12 angle of 121.7 (3)° is similar to that found previously in amidinate salts, *e.g.* in isopropylamidinium chloride [120.4 (4)°; Barker & Powell, 1996].

The C3—S2 bond length [1.815 (3) Å] is similar to that of a paraffinic C—S bond [1.816 (13) Å; Allen *et al.*, 1987], indicating little delocalization from the S atom to the aromatic ring. However, the  $C_{amidine}-S$  bond length is rather shorter [C1—S2 1.737 (3) Å] and hence it does show delocalized character, being intermediate between a single bond and the length of C=S bonds in thioureas [1.68 (2) Å; Allen *et al.*, 1987]. The N11—C1—S2 angle of 123.1 (2)° is typical of those found for an N—C=S system [122 (3)° from 1006 N—C=S fragments (all atoms acyclic) in the April 1997 edition of the CSD], but N12—C1—S2 is

115.1 (2)°; the reason for this disparity is not clear, but as the total of the three angles about C1 is 359.1°, it is likely to be due to packing rather than electronic or steric effects. [It should be noted that there are no clear differences in the chemical environments of the N, C or S atoms in the CSD sample.] The near tetrahedral C1—S2—C3 angle of 103.7 (1)° suggests hybridization of the S atom approaching  $sp^3$ . In conclusion, the N—C(S)—N fragment appears to have delocalized guanidinium character rather than amidinium character.

As might be expected, the *S*-benzylisothiuronium fragment is hydrogen bonded through both pairs of N—H atoms to Cl<sup>-</sup> ions in the lattice (Table 2). There are two short contacts which result in the formation of a virtual dimer [Cl1<sup>i</sup>···N11 3.154 (3) and Cl1<sup>i</sup>···N12<sup>i</sup> 3.191 (3) Å; symmetry code: (i)  $1 - x, -y, 1 - z$ ] (Fig. 1 and Table 2), but two longer N···Cl distances between other molecules [Cl1<sup>ii</sup>···N11<sup>ii</sup> 3.315 (3) and Cl1<sup>iii</sup>···N12<sup>iii</sup>

3.279 (3) Å; symmetry codes: (ii)  $\frac{1}{2} + x, y, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} - x, -y, z - \frac{1}{2}$ ] extend the association so that there are hydrogen-bonded layers running parallel to the *ac* plane throughout the lattice (Fig. 2).

## Experimental

The title compound was provided by the Associated Ocelt Company Ltd. Crystals were obtained by slow evaporation of an acetone solution in the dark under a nitrogen atmosphere.

### Crystal data

$C_8H_{11}N_2S^+ \cdot Cl^-$   
 $M_r = 202.70$   
 Orthorhombic  
*Pbca*  
 $a = 8.413 (1) \text{ \AA}$   
 $b = 20.534 (2) \text{ \AA}$   
 $c = 11.360 (1) \text{ \AA}$   
 $V = 1962.4 (4) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.37 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Cu  $K\alpha$  radiation  
 $\lambda = 1.5418 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 59.0\text{--}59.8^\circ$   
 $\mu = 5.04 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Plate  
 $0.30 \times 0.20 \times 0.10 \text{ mm}$   
 Yellow

### Data collection

Rigaku AFC-7R diffractometer  
 $2\theta/\omega$  scans  
 Absorption correction: refined from  $\Delta F$  (Walker & Stuart, 1983)  
 $T_{\min} = 0.393, T_{\max} = 0.604$   
 5447 measured reflections  
 2338 independent reflections

1286 reflections with  $I > 3\sigma(I)$   
 $R_{\text{int}} = 0.09$   
 $\theta_{\max} = 74.85^\circ$   
 $h = -1 \rightarrow 14$   
 $k = -25 \rightarrow 25$   
 $l = -1 \rightarrow 10$   
 3 standard reflections every 100 reflections  
 intensity decay: 10.39%

### Refinement

Refinement on  $F^2$   
 $R = 0.042$   
 $wR = 0.050$   
 $S = 1.086$   
 1286 reflections  
 109 parameters  
 H atoms: see below  
 Weighting scheme: Chebyshev polynomial (Carruthers & Watkin, 1979)

$(\Delta/\sigma)_{\max} = 0.0003$   
 $\Delta\rho_{\max} = 0.72 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$   
 Extinction correction: Larson (1970)  
 Extinction coefficient: 37 (8)  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

|           |           |            |           |
|-----------|-----------|------------|-----------|
| S2—C1     | 1.737 (3) | N11—C1     | 1.306 (4) |
| S2—C3     | 1.815 (3) | N12—C1     | 1.308 (4) |
| C1—S2—C3  | 103.7 (1) | N11—C1—N12 | 121.7 (3) |
| S2—C1—N11 | 123.1 (2) | S2—C3—C31  | 115.1 (2) |
| S2—C1—N12 | 115.1 (2) |            |           |

Table 2. Contact distances (Å)

|  |           |                          |           |
|--|-----------|--------------------------|-----------|
| Cl1...N11  | 3.154 (3) | Cl1...N11 <sup>ii</sup>  | 3.315 (3) |
| Cl1...N12 <sup>i</sup>   | 3.191 (3) | Cl1...N12 <sup>iii</sup> | 3.279 (3) |
| Symmetry codes: (i) $1 - x, -y, 1 - z$ ; (ii) $\frac{1}{2} + x, y, \frac{1}{2} - z$ ; (iii) $\frac{1}{2} - x, -y, z - \frac{1}{2}$ . |           |                          |           |

The *DIFABS* semi-empirical absorption correction was applied as the crystal had unsuitable morphology for either an azimuthal scan correction or an analytical correction based on crystal-face measurement. All non-H atom coordinates and anisotropic displacement parameters were refined freely. H atoms were placed geometrically after each cycle; isotropic displacement parameters were refined in two groups, one for aromatic ring H atoms and one for aliphatic H atoms.

Data collection: *AFC-7R Processing Software* (Molecular Structure Corporation, 1993a). Cell refinement: *AFC-7R Processing Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1211). Services for accessing these data are described at the back of the journal.

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