

(3*RS*)-S-[1-(3-Chlorophenyl)-2-oxopyrrolidin-3-yl]thiuronium bromideJiří Hanusek,^{a*} Miloš Sedlák,^a Pavel Drabina^a and Aleš Ružička^b

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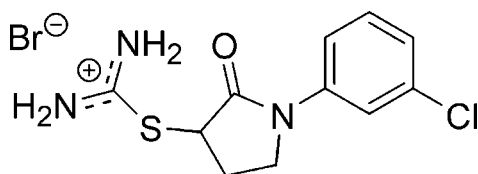
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.050; wR factor = 0.096; data-to-parameter ratio = 18.9.

In the title molecular salt, $\text{C}_{11}\text{H}_{13}\text{ClN}_3\text{OS}^+\cdot\text{Br}^-$, the C—N bond lengths in the $-\text{S}-\text{C}(\text{NH}_2)_2$ fragment indicate partial double-bond character of these bonds. The constituent ions are connected by $\text{N}-\text{H}\cdots\text{Br}$ bridges into Z-shaped chains. The supramolecular architecture of the structure can be described by being composed of these chains interlocked by additional $\text{C}-\text{H}\cdots\text{Br}$ short contacts. An intramolecular $\text{N}-\text{H}\cdots\text{O}=\text{C}$ bridge, as well as weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, are also present in the structure.

Related literature

For the preparation and reactivity of isothiuronium salts, see: Hanusek *et al.* (2004); Sedlák *et al.* (2002, 2003). For related structures, see: Bel'skii *et al.* (1985); Cotton *et al.* (2006); Hanusek *et al.* (2009); Ishii *et al.* (2000); L'abbe *et al.* (1980); Luger *et al.* (1996); Rovnyak *et al.* (1995); Vijayan & Mani (1977).

**Experimental***Crystal data*

$\text{C}_{11}\text{H}_{13}\text{ClN}_3\text{OS}^+\cdot\text{Br}^-$
 $M_r = 350.66$
Monoclinic, $P2_1/c$
 $a = 15.7379$ (9) Å
 $b = 6.4250$ (5) Å
 $c = 15.0531$ (7) Å
 $\beta = 117.329$ (5)°

$V = 1352.22$ (16) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 3.38$ mm⁻¹
 $T = 150$ (2) K
 $0.29 \times 0.12 \times 0.03$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: gaussian (Coppens, 1970)
 $T_{\min} = 0.542$, $T_{\max} = 0.873$

15769 measured reflections
3095 independent reflections
2214 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.097$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.096$
 $S = 1.15$
3095 reflections

164 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.48$ e Å⁻³
 $\Delta\rho_{\min} = -0.47$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2A}-\text{H2AB}\cdots\text{Br1}$	0.88	2.43	3.290 (3)	166
$\text{N2A}-\text{H2AA}\cdots\text{Br1}^{\text{i}}$	0.88	2.68	3.452 (3)	147
$\text{N2A}-\text{H2AA}\cdots\text{Br1}^{\text{ii}}$	0.88	2.91	3.426 (3)	119
$\text{N3A}-\text{H3AA}\cdots\text{Br1}^{\text{i}}$	0.88	2.44	3.273 (3)	158
$\text{N3A}-\text{H3AB}\cdots\text{O1}$	0.88	2.12	2.823 (4)	137
$\text{C2}-\text{H2A}\cdots\text{O1}^{\text{iii}}$	0.99	2.57	3.352 (5)	137
$\text{C3}-\text{H3B}\cdots\text{Br1}^{\text{iv}}$	0.99	3.01	3.737 (4)	131
$\text{C10}-\text{H10}\cdots\text{O1}$	0.95	2.22	2.852 (5)	124

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y+1, z$; (iv) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2122).

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(3*RS*)-*S*-[1-(3-Chlorophenyl)-2-oxopyrrolidin-3-yl]thiuronium bromide

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Comment

In our previous papers (Sedlák *et al.*, 2002, 2003; Hanusek *et al.*, 2004) we have reported that substituted *S*-(1-phenylpyrrolidin-2-on-3-yl)isothiuronium salts undergo an intramolecular recyclization reaction in a weak basic medium. During this reaction the γ -lactam cycle is split while a thiazolidine cycle, *i.e.* a substituted 2-imino-5-[2-(phenylamino)ethyl]thiazolidin-4-one, is formed.

A further interest has been provoked by a discovery (Sedlák *et al.*, 2002, 2003; Hanusek *et al.*, 2004) that *N*-unsubstituted isothiuronium salts undergo a transformation involving only a general base catalysis whereas in the case of *N,N'*-dimethylisothiuronium salts such a transformation is catalyzed by both acid and base buffer components.

In continuation of our above mentioned studies, the crystal structures of (3*RS*)-*S*-[1-(3-chlorophenyl)pyrrolidin-2-on-3-yl]isothiuronium bromide (Scheme 1, Figs. 1-3) and its *N,N'*-dimethyl derivative (Hanusek *et al.*, 2009) were determined and the influence of the methyl substituents bound to the isothiuronium moiety was examined.

There is a limited number of X-ray structures of isothiuronium salts reported in the literature. Eleven of these are the compounds of the S–C(NH₂)₂ type with no replacement of the hydrogens that are pertinent to the –NH₂ group (*e.g.* Vijayan *et al.*, 1977; Bel'skii *et al.*, 1985; Ishii *et al.*, 2000). The rest are the compounds where both nitrogen atoms are connected to a chain thus forming five- to eight-membered rings (*e.g.* Rovnyak *et al.*, 1995; Cotton *et al.*, 2006; Luger *et al.*, 1996). There is only one example of a disubstituted acyclic species, *N*-methyl- *N'*-phenyl-*S*-sulfomethylisothiourea (L'abbe *et al.*, 1980).

In the title structure and its *N,N'*-dimethyl derivative the respective interplanar angles between the S–C(NHR)₂ group and the heterocyclic rings are almost the same: 66.7 (1)° and 71.3 (1)°. The S1–C11 distance (1.749 (4) Å) in the title structure fits to the literature range 1.717–1.760 Å - *cf.* 1.770 (4) Å in *N,N'*-dimethyl derivative. The C11–N2 and C11–N3 distances also agree to the literature range that is 1.258 - 1.326 Å. (In the title compound these distances are 1.312 (5), 1.296 (5) Å, respectively, while in the *N,N'*-dimethyl derivative these distances are 1.308 (5), 1.308 (5) Å, respectively).

These C–N bond lengths in the S–C(NH₂)₂ fragment of the title structure reveal a partly double bond character of these bonds. This is in accordance with planarity of this fragment. (The groups –NH₂ were therefore duly constrained during refinement.)

The interatomic angles C4–S1–C11 (104.56 (18)°) and N2–C11–N3 (122.0 (4)°) in the title compound are similar to those in the related *N,N'*-dimethyl derivative (98.75 (18)° and 122.6 (4)°, respectively) and also fall into the literature range which is 99.2–105.5° and 108.0–123.5°, respectively. The twist angles about the N1–C5 bonds, which show a mutual orientation of both rings, are 7.8 (1) and 29.7 (1)° in the title compound and its *N,N'*-dimethyl derivative, respectively.

All the known isothiuronium cations reveal hydrogen bonding in the crystal structure. Also in the packing of the molecules of the title compound and its *N,N'*-dimethyl derivative such interactions are present. All the NH₂ hydrogen atoms are donated to the bromine atoms except for H3AB. Those with the shortest Br···H distances form infinite chains *via* the

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N2-H2AB...Br...H3AA-N3 motifs (Figs. 2 and 3; Tab. 1) with the angle H2AB...Br1...H3AA equal to 100.7 (1)°. There is also present an intramolecular N-H...O=C contact (Tab. 1, Fig. 2). The crystal packing can be described as H-bonded interlocked Z- shaped ribbons caused by the presence of additional short contacts C-H...Br (Fig. 3).

Experimental

The title compound was synthesized according to Hanusek *et al.* (2004) from saturated acetone solutions of the racemic 3-bromo-1-(3-chlorophenyl)pyrrolidin-2-one and thiourea. Suitable single crystals (plates) were grown directly from the reaction mixture. Their average size was 0.2×0.1×0.02 mm.

Refinement

All the hydrogens were discernible in the difference electron density map. However, all the hydrogens were situated into idealized positions and refined riding on their parent C or N atoms, with N-H = 0.88 Å, $U(H) = 1.2U_{eq}(C)$, C-H = 0.95 Å (for aryl H), C-H = 0.99 Å for methylene and C-H = 1.00 Å for methine, $U(H) = 1.2U_{eq}(C/N)$ for the amine, methylene and methine H atoms, respectively.

Figures

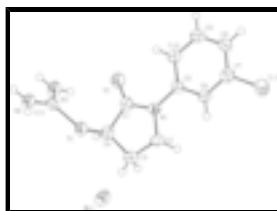


Fig. 1. View of the title molecule with the displacement ellipsoids shown on 50% probability level. The H atoms are shown with arbitrary radius.

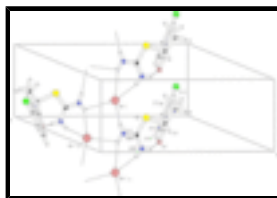


Fig. 2. View of the motif of the structure with the hydrogen bonding.

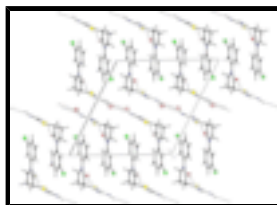


Fig. 3. View of the unit cell along the axis c. The H bonding is depicted. Symmetry codes for Br1c: x, -1+y, z; for Br1d: 1-x, -1/2+y, 3/2-z; for another isothiuronium fragment: x, 1+y, z.

(3*RS*)-*S*-[1-(3-Chlorophenyl)-2-oxopyrrolidin-3-yl]thiuronium bromide

Crystal data

$C_{11}H_{13}ClN_3OS^+Br^-$

$M_r = 350.66$

Monoclinic, $P2_1/c$

$F_{000} = 704$

$D_x = 1.722 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Hall symbol: -P 2ybc
 $a = 15.7379$ (9) Å
 $b = 6.4250$ (5) Å
 $c = 15.0531$ (7) Å
 $\beta = 117.329$ (5)°
 $V = 1352.22$ (16) Å³
 $Z = 4$

Cell parameters from 15779 reflections
 $\theta = 1-27.5^\circ$
 $\mu = 3.38$ mm⁻¹
 $T = 150$ (2) K
 Plate, colourless
 $0.29 \times 0.12 \times 0.03$ mm

Data collection

Bruker–Nonius KappaCCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Monochromator: graphite
 Detector resolution: 9.091 pixels mm⁻¹
 $T = 150$ (1) K
 φ and ω scans
 Absorption correction: gaussian
 (Coppens, 1970)
 $T_{\min} = 0.542$, $T_{\max} = 0.873$
 15769 measured reflections

3095 independent reflections
 2214 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.097$
 $\theta_{\text{max}} = 27.5^\circ$
 $\theta_{\text{min}} = 2.9^\circ$
 $h = -20 \rightarrow 20$
 $k = -7 \rightarrow 8$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.096$
 $S = 1.15$
 3095 reflections
 164 parameters
 52 constraints
 Primary atom site location: structure-invariant direct
 methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: difference Fourier map
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 1.6718P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0036 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculat-

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ing R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.48049 (3)	0.45589 (6)	0.65892 (3)	0.04086 (16)
S1	0.34553 (7)	0.14593 (15)	0.41198 (8)	0.0339 (2)
Cl1	-0.19436 (7)	0.30572 (19)	-0.02926 (9)	0.0532 (3)
O1	0.21265 (19)	-0.2562 (4)	0.2711 (2)	0.0450 (7)
C5	0.0464 (3)	0.0076 (6)	0.1482 (3)	0.0295 (8)
C6	-0.0184 (3)	0.1577 (6)	0.0890 (3)	0.0330 (9)
H6	0.0040	0.2871	0.0774	0.040*
C4	0.3119 (3)	0.0455 (6)	0.2870 (3)	0.0346 (9)
H4	0.3640	-0.0404	0.2852	0.042*
C11	0.3880 (2)	-0.0716 (6)	0.4901 (3)	0.0291 (8)
C2	0.1792 (3)	0.2598 (6)	0.1780 (3)	0.0372 (10)
H2A	0.1660	0.3657	0.2179	0.045*
H2B	0.1480	0.3027	0.1069	0.045*
C1	0.2191 (3)	-0.0747 (6)	0.2493 (3)	0.0329 (9)
C10	0.0120 (3)	-0.1790 (7)	0.1662 (3)	0.0398 (10)
H10	0.0552	-0.2828	0.2072	0.048*
C8	-0.1500 (3)	-0.0645 (7)	0.0639 (3)	0.0422 (10)
H8	-0.2169	-0.0891	0.0349	0.051*
C7	-0.1148 (3)	0.1186 (7)	0.0473 (3)	0.0375 (9)
C9	-0.0854 (3)	-0.2119 (7)	0.1239 (3)	0.0459 (11)
H9	-0.1085	-0.3394	0.1364	0.055*
C3	0.2862 (3)	0.2309 (7)	0.2163 (3)	0.0410 (10)
H3A	0.3216	0.3568	0.2522	0.049*
H3B	0.3012	0.2018	0.1605	0.049*
N2A	0.4287 (2)	-0.0308 (5)	0.5862 (2)	0.0359 (8)
H2AA	0.4517	-0.1329	0.6299	0.043*
H2AB	0.4331	0.0986	0.6070	0.043*
N1	0.1455 (2)	0.0527 (5)	0.1902 (2)	0.0301 (7)
N3A	0.3800 (2)	-0.2598 (5)	0.4563 (3)	0.0387 (8)
H3AA	0.4023	-0.3650	0.4982	0.046*
H3AB	0.3523	-0.2825	0.3914	0.046*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0583 (3)	0.0267 (2)	0.0360 (2)	-0.00529 (19)	0.0203 (2)	-0.00053 (19)
S1	0.0371 (5)	0.0258 (5)	0.0328 (5)	0.0008 (4)	0.0109 (4)	-0.0016 (4)
Cl1	0.0390 (6)	0.0562 (7)	0.0584 (7)	0.0075 (5)	0.0172 (5)	0.0116 (6)
O1	0.0468 (17)	0.0269 (16)	0.0439 (18)	-0.0033 (13)	0.0059 (13)	0.0010 (13)
C5	0.032 (2)	0.030 (2)	0.027 (2)	-0.0057 (15)	0.0133 (16)	-0.0075 (16)
C6	0.036 (2)	0.030 (2)	0.034 (2)	-0.0026 (17)	0.0161 (17)	0.0017 (17)
C4	0.034 (2)	0.037 (2)	0.032 (2)	-0.0007 (18)	0.0144 (17)	0.0001 (19)

C11	0.0234 (18)	0.025 (2)	0.039 (2)	-0.0001 (15)	0.0141 (16)	-0.0007 (17)
C2	0.037 (2)	0.030 (2)	0.040 (2)	-0.0071 (17)	0.0141 (18)	0.0067 (18)
C1	0.038 (2)	0.030 (2)	0.027 (2)	0.0000 (17)	0.0123 (17)	-0.0043 (17)
C10	0.040 (2)	0.036 (2)	0.038 (2)	-0.0058 (18)	0.0143 (19)	0.0043 (19)
C8	0.035 (2)	0.056 (3)	0.034 (2)	-0.014 (2)	0.0140 (18)	-0.002 (2)
C7	0.038 (2)	0.043 (2)	0.033 (2)	0.0007 (19)	0.0176 (18)	-0.0003 (19)
C9	0.048 (2)	0.041 (3)	0.047 (3)	-0.015 (2)	0.020 (2)	0.004 (2)
C3	0.038 (2)	0.048 (3)	0.038 (2)	-0.0066 (19)	0.0177 (19)	0.007 (2)
N2A	0.0434 (19)	0.0261 (16)	0.0307 (19)	-0.0003 (15)	0.0104 (15)	-0.0017 (15)
N1	0.0291 (16)	0.0265 (16)	0.0319 (18)	-0.0045 (14)	0.0116 (14)	-0.0010 (14)
N3A	0.049 (2)	0.0262 (18)	0.0327 (19)	0.0049 (15)	0.0117 (16)	-0.0026 (15)

Geometric parameters (Å, °)

S1—C11	1.749 (4)	C2—H2A	0.9900
S1—C4	1.822 (4)	C2—H2B	0.9900
C11—C7	1.737 (4)	C1—N1	1.363 (5)
O1—C1	1.228 (4)	C10—C9	1.379 (6)
C5—C6	1.389 (5)	C10—H10	0.9500
C5—C10	1.392 (5)	C8—C7	1.371 (6)
C5—N1	1.418 (4)	C8—C9	1.380 (6)
C6—C7	1.374 (5)	C8—H8	0.9500
C6—H6	0.9500	C9—H9	0.9500
C4—C1	1.514 (5)	C3—H3A	0.9900
C4—C3	1.523 (5)	C3—H3B	0.9900
C4—H4	1.0000	N2A—H2AA	0.8800
C11—N3A	1.296 (5)	N2A—H2AB	0.8800
C11—N2A	1.312 (5)	N3A—H3AA	0.8800
C2—N1	1.475 (5)	N3A—H3AB	0.8800
C2—C3	1.520 (5)		
C11—S1—C4	104.56 (18)	C9—C10—H10	120.3
C6—C5—C10	119.1 (3)	C5—C10—H10	120.3
C6—C5—N1	118.5 (3)	C7—C8—C9	118.0 (4)
C10—C5—N1	122.4 (3)	C7—C8—H8	121.0
C7—C6—C5	119.9 (4)	C9—C8—H8	121.0
C7—C6—H6	120.1	C8—C7—C6	121.9 (4)
C5—C6—H6	120.1	C8—C7—C11	119.1 (3)
C1—C4—C3	103.7 (3)	C6—C7—C11	119.0 (3)
C1—C4—S1	109.9 (3)	C10—C9—C8	121.8 (4)
C3—C4—S1	107.6 (3)	C10—C9—H9	119.1
C1—C4—H4	111.8	C8—C9—H9	119.1
C3—C4—H4	111.8	C2—C3—C4	104.7 (3)
S1—C4—H4	111.8	C2—C3—H3A	110.8
N3A—C11—N2A	122.0 (4)	C4—C3—H3A	110.8
N3A—C11—S1	122.9 (3)	C2—C3—H3B	110.8
N2A—C11—S1	115.1 (3)	C4—C3—H3B	110.8
N1—C2—C3	104.0 (3)	H3A—C3—H3B	108.9
N1—C2—H2A	111.0	C11—N2A—H2AA	120.0
C3—C2—H2A	111.0	C11—N2A—H2AB	120.0

supplementary materials

N1—C2—H2B	111.0	H2AA—N2A—H2AB	120.0
C3—C2—H2B	111.0	C1—N1—C5	126.8 (3)
H2A—C2—H2B	109.0	C1—N1—C2	112.1 (3)
O1—C1—N1	126.5 (4)	C5—N1—C2	120.9 (3)
O1—C1—C4	124.6 (4)	C11—N3A—H3AA	120.0
N1—C1—C4	108.8 (3)	C11—N3A—H3AB	120.0
C9—C10—C5	119.4 (4)	H3AA—N3A—H3AB	120.0

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2A—H2AB \cdots Br1	0.88	2.43	3.290 (3)	166
N2A—H2AA \cdots Br1 ⁱ	0.88	2.68	3.452 (3)	147
N2A—H2AA \cdots Br1 ⁱⁱ	0.88	2.91	3.426 (3)	119
N3A—H3AA \cdots Br1 ⁱ	0.88	2.44	3.273 (3)	158
N3A—H3AB \cdots O1	0.88	2.12	2.823 (4)	137
C2—H2A \cdots O1 ⁱⁱⁱ	0.99	2.57	3.352 (5)	137
C3—H3B \cdots Br1 ^{iv}	0.99	3.01	3.737 (4)	131
C10—H10 \cdots O1	0.95	2.22	2.852 (5)	124

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, y-1/2, -z+3/2$; (iii) $x, y+1, z$; (iv) $x, -y+1/2, z-1/2$.

Fig. 1

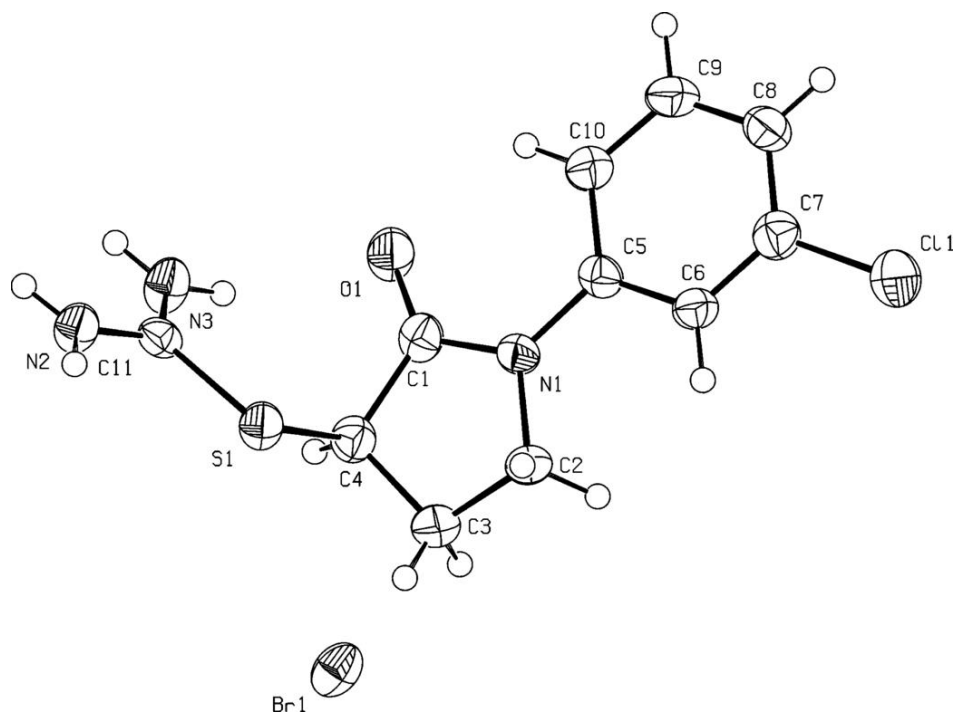


Fig. 2

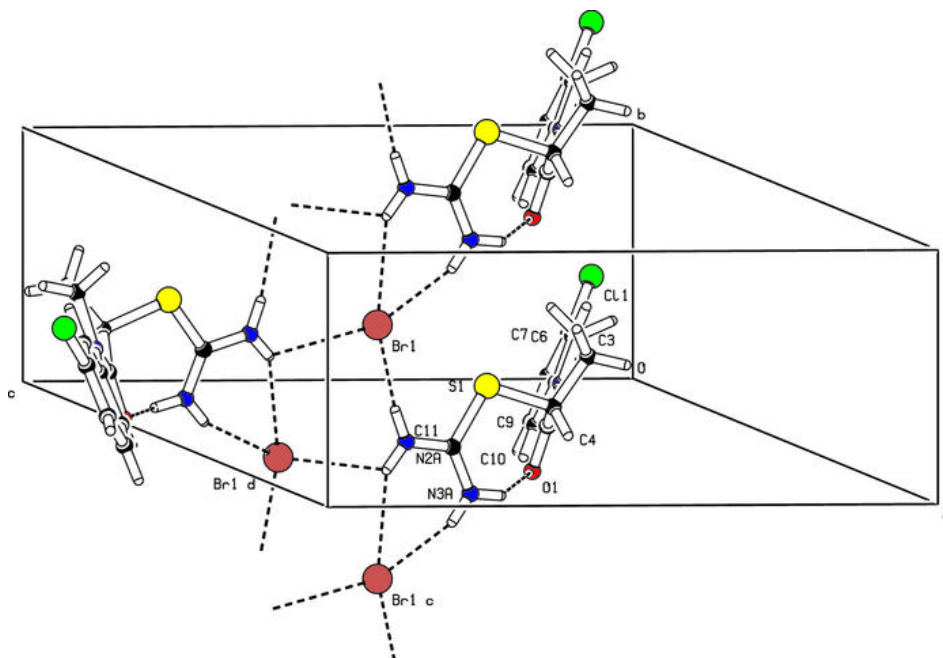


Fig. 3

