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(*E*)-2-[(2,3-Dibromoallyl)sulfanyl]-1-methyl-1*H*-imidazol-3-ium bromide

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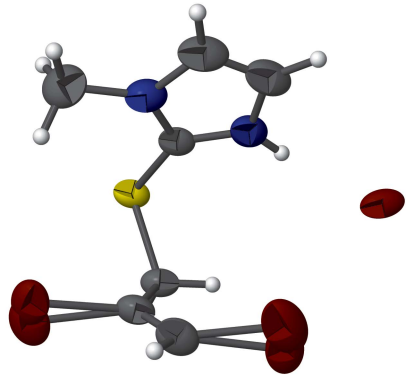
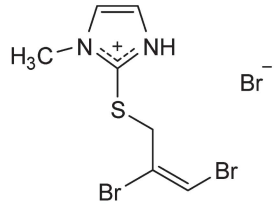
Structural data: full structural data are available from iucrdata.iucr.org

The title salt, $C_7H_9Br_2N_2S^+\cdot Br^-$, was obtained from methimazole (1-methyl-3*H*-imidazole-2-thione) by *S*-allylation using 1,2,3-tribromopropene. A positional disorder of the bromine atoms at the allyl chain was observed, with each Br atom equally disordered over two positions. N—H···Br and C—H···Br interactions were identified.

3D view



Chemical scheme



Structure description

The imidazolium ring in the title compound is almost perfectly planar [maximum deviation = 0.004 (2) Å for N2, and the *S*-allyl chain is positioned perpendicularly to the ring system, making a dihedral angle of 88.95 (13)° (Fig. 1). Atom C5 is displaced from the ring plane by 1.481 (2) Å. The cation acts as a multiple donor of hydrogen-bond contacts. Each bromide ion accepts four hydrogen bonds from four neighbouring cations (Table 1). A classical N1—H···Br3 hydrogen bond and a quite short C3—H···Br3 contact are observed. The hydrogen atoms of the allyl group are engaged in C5—H···Br and C7—H···Br interactions (Fig. 2).

A related structure without bromine atoms at the allyl chain has been reported (Gaitor *et al.*, 2015).

Synthesis and crystallization

1,2,3-Tribromopropene (0.50 g, 1.8 mmol; Kodomari *et al.*, 1989) was added to a solution of methimazole (0.25 g, 2.2 mmol) in CH_2Cl_2 (3 ml). The mixture was stirred at room temperature for 18 h. The colorless product was collected by filtration, washed with CH_2Cl_2 and dried under reduced pressure (0.47 g, 67%), m.p. 442 K. Suitable crystals were obtained by slow evaporation of a solution in EtOH. The PXRD (Mo Kα radiation) of the bulk material was identical to the one calculated from the single-crystal diffraction

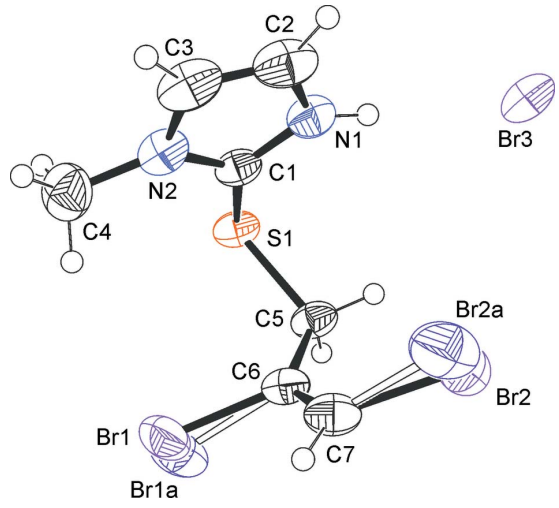


Figure 1
The molecular structure of the ion pair of the title compound, showing the atom labels and 50% probability displacement ellipsoids for the non-H atoms.

data (Fig. 3), indicating phase purity. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.88 (*s*, 3H), 4.22 (*s*, 2H), 7.06 (*s*, 1H), 7.87 (*d*, J = 1.6 Hz, 1H), 7.97 (*d*, J = 1.6 Hz, 1H) p.p.m. ^{13}C NMR (75 MHz, DMSO-d_6): δ 35.4, 41.9, 108.4, 119.6, 122.0, 126.3, 136.7 p.p.m. IR (neat): ν 3157 (*w*), 3071 (*w*), 3025 (*m*), 2890 (*w*), 2779 (*m*), 1572 (*m*), 1480 (*m*), 1293 (*m*), 1018 (*m*), 907 (*m*), 835 (*m*), 770 (*s*), 698 (*m*), 673 (*m*) cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atoms Br1 and Br2 showed extreme temperature factors and were split over two positions with a 1:1 ratio for each.

Acknowledgements

The authors are grateful to Martin Lamb for the PXRD measurements.

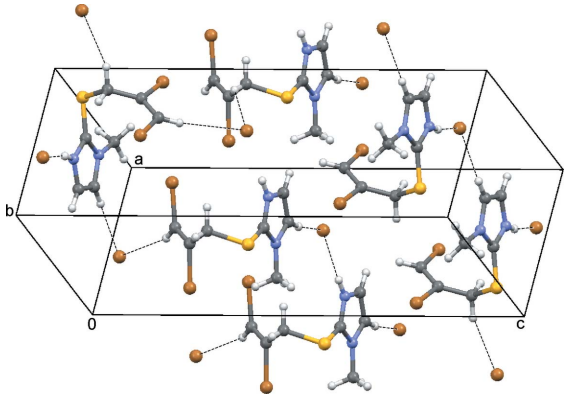


Figure 2
Crystal packing of the title compound, with hydrogen bonds drawn as dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Br3	0.85 (2)	2.37 (2)	3.215 (2)	170 (2)
C3—H3···Br3^{i}	0.95	2.64	3.584 (3)	170
C5—H5A···Br3^{ii}	0.99	2.89	3.669 (2)	136
C7—H7···Br3^{iii}	0.95	2.87	3.772 (2)	159

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_9Br_2N_2S^+\cdot Br^-$
M_r	392.95
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	203
a, b, c (Å)	7.2101 (3), 8.2105 (3), 20.5363 (8)
β (°)	90.619 (1)
V (Å^3)	1215.65 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	10.09
Crystal size (mm)	0.18 × 0.14 × 0.12
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 100
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.208, 0.333
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22243, 2513, 2228
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.628
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.052, 1.04
No. of reflections	2513
No. of parameters	142
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, −0.50

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

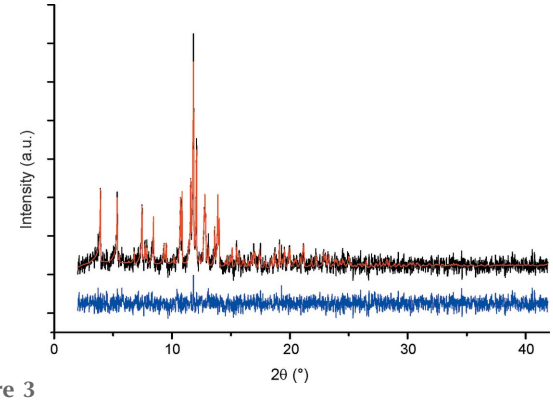


Figure 3
Pawley fit (R_{wp} = 2.77%, R_{exp} = 3.33%, R_p = 2.21%, goodness-of-fit = 0.83) of the PXRD data with a model calculated from the structural data of the single-crystal structure determination. Black dots indicate raw data, while the red line indicates the calculated model. The difference curve is shown in blue.

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full crystallographic data

IUCrData (2016). **1**, x161499 [doi:10.1107/S2414314616014991]

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Crystal data

$C_7H_9Br_2N_2S^+\cdot Br^-$
M_r = 392.95
Monoclinic, $P2_1/c$
a = 7.2101 (3) Å
b = 8.2105 (3) Å
c = 20.5363 (8) Å
β = 90.619 (1)°
V = 1215.65 (8) Å^3
Z = 4
$F(000)$ = 744
D_x = 2.147 Mg m^{-3}
Melting point: 442 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9903 reflections
θ = 2.7–26.7°
μ = 10.09 mm^{-1}
T = 203 K
Prism, colourless
0.18 × 0.14 × 0.12 mm

Data collection

Bruker D8 QUEST PHOTON 100 diffractometer
Radiation source: Incoatec Microfocus
Multi layered optics monochromator
Detector resolution: 10.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.208, T_{max} = 0.333
22243 measured reflections
2513 independent reflections
2228 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 26.5°, θ_{min} = 2.7°
h = −9→8
k = −10→10
l = −25→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.052
S = 1.04
2513 reflections
142 parameters
1 restraint
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2 + 0.5418P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0054 (4)

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. Hydrogen at N1 found and refined isotropically with bond restraints (d=87 pm). The two Br-Atoms Br1 and shows extremly cigarlikes temperature factors and were split in two position with ratio of 1:1 for each.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.17108 (7)	0.46260 (6)	0.42687 (2)	0.03705 (13)	
N1	0.5433 (3)	0.3906 (2)	0.42723 (9)	0.0423 (4)	
H1	0.588 (3)	0.487 (2)	0.4262 (12)	0.047 (7)*	
N2	0.3706 (3)	0.1773 (2)	0.42235 (9)	0.0424 (4)	
C1	0.3676 (3)	0.3405 (2)	0.42357 (9)	0.0355 (5)	
C2	0.6586 (4)	0.2590 (3)	0.42872 (13)	0.0546 (7)	
H2	0.7902	0.2612	0.4312	0.066*	
C3	0.5518 (4)	0.1265 (3)	0.42602 (12)	0.0542 (6)	
H3	0.5935	0.0167	0.4266	0.065*	
C4	0.2091 (4)	0.0698 (3)	0.42008 (14)	0.0593 (7)	
H4A	0.1409	0.0790	0.4609	0.089*	
H4B	0.2501	−0.0430	0.4142	0.089*	
H4C	0.1281	0.1013	0.3836	0.089*	
C5	0.1903 (3)	0.5685 (3)	0.34904 (10)	0.0387 (5)	
H5A	0.0911	0.6516	0.3462	0.046*	
H5B	0.3107	0.6263	0.3482	0.046*	
C6	0.1770 (3)	0.4618 (3)	0.29077 (10)	0.0391 (5)	
C7	0.2959 (3)	0.4451 (3)	0.24341 (11)	0.0482 (6)	
H7	0.2764	0.3655	0.2105	0.058*	
Br1	−0.0306 (4)	0.3200 (3)	0.28492 (17)	0.0617 (5)	0.5
Br2	0.5085 (3)	0.58268 (18)	0.24163 (10)	0.0641 (3)	0.5
Br1A	−0.0598 (5)	0.3638 (3)	0.27945 (17)	0.0629 (5)	0.5
Br2A	0.5379 (3)	0.5213 (2)	0.24649 (11)	0.0788 (5)	0.5
Br3	0.76128 (4)	0.73127 (3)	0.41814 (2)	0.04785 (10)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0432 (3)	0.0407 (3)	0.0273 (3)	0.0116 (2)	0.0008 (2)	−0.0028 (2)
N1	0.0437 (11)	0.0469 (11)	0.0364 (10)	0.0067 (9)	0.0020 (8)	0.0030 (8)
N2	0.0560 (12)	0.0365 (9)	0.0346 (10)	0.0114 (9)	0.0038 (8)	−0.0037 (8)
C1	0.0436 (12)	0.0391 (11)	0.0238 (10)	0.0077 (9)	0.0006 (8)	−0.0013 (8)
C2	0.0477 (14)	0.0711 (18)	0.0452 (14)	0.0241 (13)	0.0046 (11)	0.0029 (12)
C3	0.0664 (16)	0.0520 (14)	0.0442 (14)	0.0275 (13)	0.0067 (11)	0.0003 (11)
C4	0.0742 (18)	0.0436 (14)	0.0601 (17)	−0.0037 (12)	0.0025 (13)	−0.0073 (11)
C5	0.0520 (13)	0.0351 (11)	0.0289 (10)	0.0094 (9)	−0.0022 (9)	−0.0022 (8)
C6	0.0468 (12)	0.0402 (11)	0.0301 (11)	0.0079 (9)	−0.0058 (9)	−0.0013 (9)
C7	0.0531 (14)	0.0583 (14)	0.0332 (12)	0.0081 (11)	−0.0031 (10)	−0.0075 (10)
Br1	0.0635 (11)	0.0797 (12)	0.0418 (5)	−0.0244 (8)	−0.0079 (7)	−0.0081 (8)
Br2	0.0551 (7)	0.0919 (9)	0.0454 (4)	−0.0165 (6)	0.0079 (4)	−0.0053 (6)
Br1A	0.0572 (7)	0.0840 (13)	0.0472 (9)	−0.0074 (7)	−0.0048 (5)	−0.0183 (9)
Br2A	0.0574 (6)	0.1289 (14)	0.0501 (6)	−0.0017 (8)	0.0080 (4)	−0.0115 (9)

Br3	0.07191 (18)	0.03746 (13)	0.03436 (14)	0.01620 (10)	0.00936 (10)	0.00275 (9)

Geometric parameters (Å, º)

S1—C1	1.738 (2)	C4—H4B	0.9800
S1—C5	1.826 (2)	C4—H4C	0.9800
N1—C1	1.333 (3)	C5—C6	1.485 (3)
N1—C2	1.364 (3)	C5—H5A	0.9900
N1—H1	0.852 (16)	C5—H5B	0.9900
N2—C1	1.340 (3)	C6—C7	1.311 (3)
N2—C3	1.372 (3)	C6—Br1A	1.899 (4)
N2—C4	1.462 (3)	C6—Br1	1.899 (4)
C2—C3	1.334 (4)	C7—Br2A	1.854 (3)
C2—H2	0.9500	C7—Br2	1.905 (3)
C3—H3	0.9500	C7—H7	0.9500
C4—H4A	0.9800		
C1—S1—C5	99.84 (10)	N2—C4—H4C	109.5
C1—N1—C2	109.6 (2)	H4A—C4—H4C	109.5
C1—N1—H1	130.1 (17)	H4B—C4—H4C	109.5
C2—N1—H1	120.2 (17)	C6—C5—S1	114.81 (15)
C1—N2—C3	108.6 (2)	C6—C5—H5A	108.6
C1—N2—C4	126.3 (2)	S1—C5—H5A	108.6
C3—N2—C4	125.1 (2)	C6—C5—H5B	108.6
N1—C1—N2	107.10 (18)	S1—C5—H5B	108.6
N1—C1—S1	126.47 (16)	H5A—C5—H5B	107.5
N2—C1—S1	126.21 (17)	C7—C6—C5	128.5 (2)
C3—C2—N1	107.1 (2)	C7—C6—Br1A	117.3 (2)
C3—C2—H2	126.5	C5—C6—Br1A	113.50 (19)
N1—C2—H2	126.5	C7—C6—Br1	114.2 (2)
C2—C3—N2	107.6 (2)	C5—C6—Br1	117.17 (19)
C2—C3—H3	126.2	C6—C7—Br2A	124.2 (2)
N2—C3—H3	126.2	C6—C7—Br2	119.02 (19)
N2—C4—H4A	109.5	C6—C7—H7	120.5
N2—C4—H4B	109.5	Br2—C7—H7	120.5
H4A—C4—H4B	109.5		
C2—N1—C1—N2	−0.3 (2)	C1—N2—C3—C2	−0.7 (3)
C2—N1—C1—S1	174.60 (17)	C4—N2—C3—C2	−178.5 (2)
C3—N2—C1—N1	0.6 (2)	C1—S1—C5—C6	63.61 (18)
C4—N2—C1—N1	178.4 (2)	S1—C5—C6—C7	−123.8 (2)
C3—N2—C1—S1	−174.33 (16)	S1—C5—C6—Br1A	66.0 (2)
C4—N2—C1—S1	3.5 (3)	S1—C5—C6—Br1	52.2 (2)
C5—S1—C1—N1	69.29 (19)	C5—C6—C7—Br2A	13.5 (4)
C5—S1—C1—N2	−116.71 (18)	Br1A—C6—C7—Br2A	−176.56 (15)
C1—N1—C2—C3	−0.1 (3)	C5—C6—C7—Br2	−5.4 (3)
N1—C2—C3—N2	0.5 (3)	Br1—C6—C7—Br2	178.56 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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C3—H3···Br3^{i}	0.95	2.64	3.584 (3)	170
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