Electronic Supporting Information (ESI)

A Unique Case of Polymorphism in Polyiodide Networks Resulting from the Reaction of the Drug Methimazole and I_2.

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Table S1. Crystallographic data and structure refinement details for **1-triclinic**.

Compound	$[2(C_4H_5N_2S\text{-}SN_2C_4H_6)]I_3I_5$
Formula	$C_{16}H_{22}I_8N_8S_4$
Crystal system	triclinic
Space group	*P*-1 (no. 2)
M.*W*.	1469.85
a / Å	7.0461(9)
b / Å	11.5109 (14)
c / Å	23.868(3)
α / º	91.44(1)
β / º	92.78(1)
γ / º	102.42(1)
V / Å^3	1887.1(4)
Z	2
D_c /g/cm^{-3}	2.587
μ/ mm^{-1}	6.817
Measured reflections	17105
Unique reflections, R_{int}	7423, 0.041
Observed reflections [$I > 2\sigma(I)$]	4776
Absorption correction	*SADABS*
T_{min}, T_{max}	0.513, 1.000
Parameters refined	325
R	0.0388
*wR*2 [all data]	0.0955
GOF	0.902
$\Delta\rho_{min}$, $\Delta\rho_{max}$ /e Å^{-3}	-1.1(1), 1.2(1)

$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$;

$GOF = \{\Sigma[w(Fo^2-Fc^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Table S2. $[2(C_4H_5N_2S\text{-}SN_2C_4H_6)]I_3I_5$ (**1-triclinic**). Selected interatomic distances (Å) and angles (deg.)

I1-I2	2.9532(8)	I1-I2-I3	178.98(2)
I2-I3	2.9019(8)	I4-I5-I6	176.63(3)
I4-I5	2.7936(9)	I5-I6-I7	96.26(2)
I5-I6	3.1134(9)	I6-I7-I8	174.79(2)
I6-I7	3.0207(8)		
I7-I8	2.8255(8)		
I1···I8	4.1238(10)	I3···I3b	4.2765(10)
I3···I3a	3.8282(11)	I4···I7c	4.3001(11)
I4···I4d	3.5752(11)	I5···I6e	4.2661(11)
I6···I6e	3.8254(11)		
S11-S21	2.088(3)	S12-S22	2.091(3)
S11-C11	1.739(7)	S12-C12	1.752(7)
S21-C51	1.750(7)	S22-C52	1.758(7)
N11-C11	1.317(8)	N12-C12	1.314(8)
N11-C31	1.350(9)	N12-C32	1.355(9)
N21-C11	1.341(8)	N22-C12	1.342(8)
N21-C21	1.354(10)	N22-C22	1.364(9)
N21-C41	1.461(10)	N22-C42	1.493(9)
N31-C51	1.317(8)	N32-C52	1.316(9)
N31-C61	1.357(10)	N32-C62	1.362(9)
N41-C51	1.346(8)	N42-C52	1.359(8)
N41-C71	1.341(10)	N42-C72	1.356(9)
N41-C81	1.476(10)	N42-C82	1.450(10)
C21-C31	1.350(11)	C22-C32	1.343(10)
C61-C71	1.342(11)	C62-C72	1.338(11)
C11-S11-S21	102.0(2)	C12-S12-S22	102.6(2)
C51-S21-S11	103.0(2)	C52-S22-S12	103.0(2)
C11-N11-C31	109.3(6)	C12-N12-C32	109.3(6)
C11-N21-C21	109.3(7)	C11-N21-C41	125.7(6)
C21-N21-C41	125.0(7)	C12-N22-C22	108.3(6)
C12-N22-C42	125.0(6)	C22-N22-C42	126.7(6)
C51-N31-C61	105.5(6)	C52-N32-C62	104.9(6)
C71-N41-C51	106.5(6)	C72-N42-C52	104.6(6)
C71-N41-C81	125.9(7)	C72-N42-C82	127.7(7)
C51-N41-C81	127.5(7)	C52-N42-C82	127.7(6)
N11-C11-N21	107.3(6)	N12-C12-N22	107.9(6)
N11-C11-S11	126.5(5)	N12-C12-S12	126.0(5)
N21-C11-S11	126.1(6)	N22-C12-S12	125.7(5)
C31-C21-N21	106.3(7)	C32-C22-N22	107.0(7)

C21-C31-N11	107.7(7)	C22-C32-N12	107.4(7)
N31-C51-N41	111.1(6)	N32-C52-N42	112.5(6)
N31-C51-S21	124.5(5)	N32-C52-S22	124.5(5)
N41-C51-S21	124.2(6)	N42-C52-S22	122.9(6)
C71-C61-N31	109.3(7)	C72-C62-N32	109.5(7)
N41-C71-C61	107.5(7)	N42-C72-C62	108.6(7)
C11-S11-S21-C51	94.3(3)	C12-S12-S22-C52	-90.6(3)

Hydrogen bonds

N12···N31	2.712(8)	N12-H12···N31	176.1(4)
N11···N32	2.690(9)	N11-H11···N32	176.4(4)

Symmetry codes: a =1 - x, 2 - y, 1 - z; b = 2 - x, 2 - y, 1 - z; c = 1 + x, y, z; d = 4-x, 1 - y, -z; e = 3 - x, 2 - y, -z.

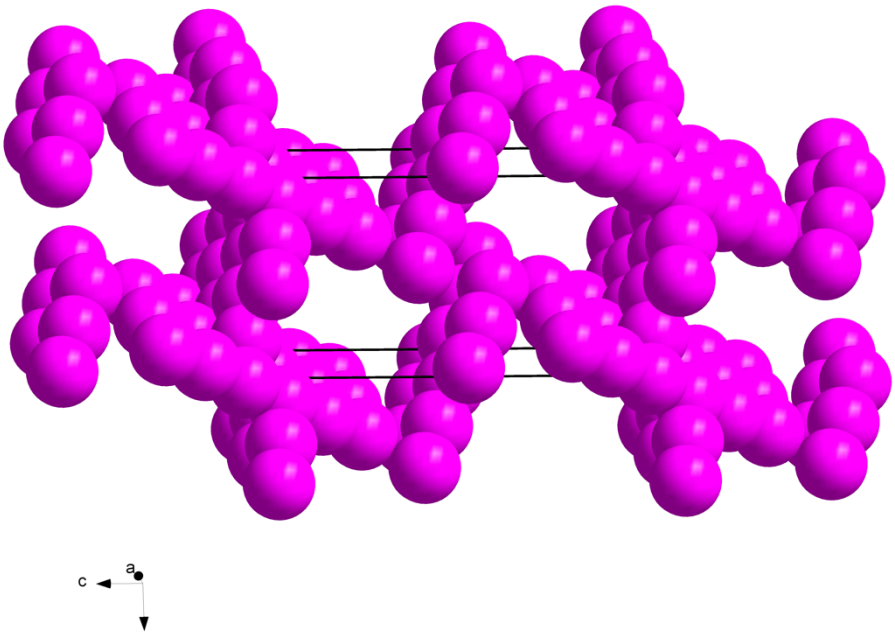

Figure S1. Compound **1-triclinic**. The iodide framework seen almost along [100]. The Iodine atoms are drawn with their van der Waals radii to show the channels where the dimeric units made by the two hydrogen-bonded independent monocations are hosted.

Cation methimazole-disulfide $[C_4H_5N_2S\text{-}SN_2C_4H_6]^+$

Name:	DA208
Formula:	$C_8H_{11}N_4S_2$

Job type:	Energy
Method:	ωB97X-D
Basis set:	6-31G*
Charge:	+1
Energy:	-1326.400982 hartrees

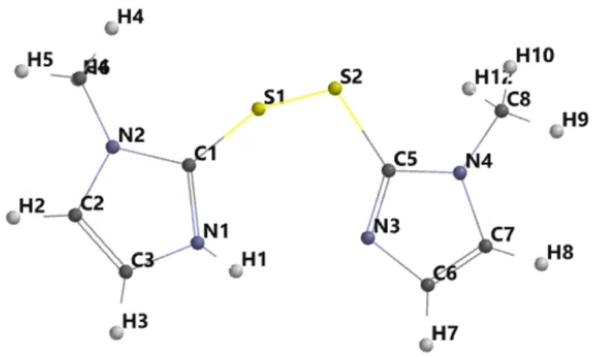

Figure S2. Cation methimazole-disulfide: atom numbering scheme.

Table S3. Cation methimazole-disulfide $[C_4H_5N_2S\text{-}SN_2C_4H_6]^+$ atomic charges (|e|).

Atom Label	Natural charge	Mulliken charge	Electrostatic charge
C1	+0.252	+0.272	+0.165
C2	-0.050	+0.025	-0.283
C3	-0.043	-0.001	+0.000
C4	-0.510	-0.413	-0.695
C5	+0.127	+0.183	+0.273
C6	-0.096	-0.078	+0.093

C7	-0.061	+0.008	-0.431
C8	-0.491	-0.383	-0.763
H1	+0.488	+0.426	+0.384
H2	+0.290	+0.271	+0.253
H3	+0.292	+0.275	+0.210
H4	+0.282	+0.254	+0.232
H5	+0.276	+0.243	+0.262
H6	+0.271	+0.245	+0.256
H7	+0.256	+0.206	+0.153
H8	+0.267	+0.235	+0.260
H9	+0.264	+0.222	+0.278
H10	+0.260	+0.225	+0.245
H12	+0.253	+0.213	+0.218
N1	-0.520	-0.512	-0.294
N2	-0.350	-0.390	+0.343
N3	-0.503	-0.438	-0.532
N4	-0.380	-0.391	+0.372
S1	+0.185	+0.135	-0.030
S2	+0.239	+0.167	+0.031

Bis-cation methimazole-disulfide $\{[C_4H_5N_2S\text{-}SN_2C_4H_6]^+\}_2$

Name:	DA208
Formula:	$2C_8H_{11}N_4S_2$

Job type:	Energy
Method:	ωB97X-D
Basis set:	6-31G*
Charge:	+2
Energy:	-2652.755824 hartrees

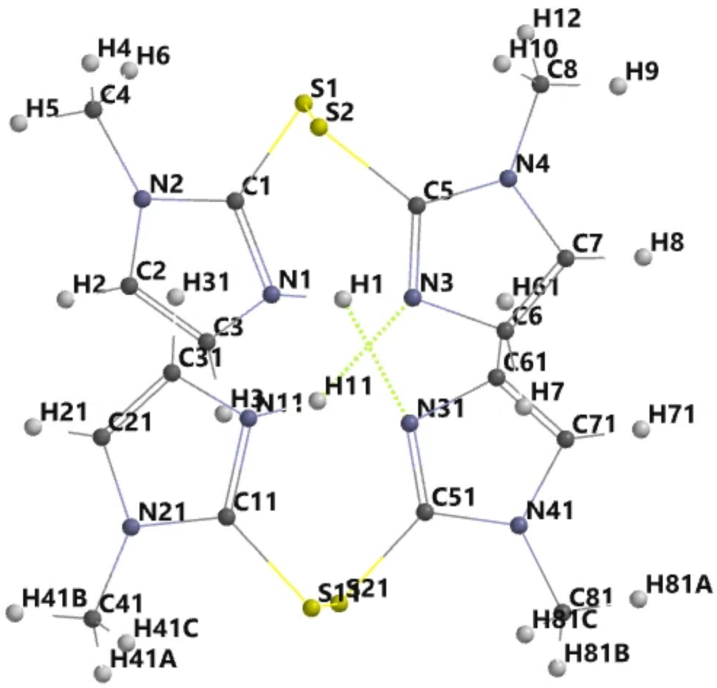

Figure S3. *Bis*-cation methimazole-disulfide: atom numbering scheme.

Table S4. *Bis*-cation methimazole disulfide $\{[C_4H_5N_2S\text{-}SN_2C_4H_6]^+\}_2$ atomic charges (|e|).

Atom Label	Natural charge	Mulliken charge	Electrostatic charge
C1	+0.231	+0.244	+0.273
C2	-0.051	+0.021	-0.205
C3	-0.036	-0.008	+0.010
C4	-0.514	-0.420	-0.613
C5	+0.156	+0.205	+0.235
C6	-0.087	-0.045	-0.023
C7	-0.055	+0.005	-0.285
C8	-0.496	-0.393	-0.755
C11	+0.242	+0.256	+0.158
C21	-0.041	+0.028	-0.310
C31	-0.048	-0.020	+0.118
C41	-0.514	-0.420	-0.590
C51	+0.144	+0.188	+0.292
C61	-0.096	-0.032	-0.049
C71	-0.056	-0.040	-0.214
C81	-0.495	-0.402	-0.594
H1	+0.493	+0.450	+0.388
H2	+0.293	+0.278	+0.245
H3	+0.298	+0.275	+0.148
H4	+0.281	+0.252	+0.211
H5	+0.281	+0.250	+0.256
H6	+0.278	+0.257	+0.256
H7	+0.246	+0.196	+0.127
H8	+0.276	+0.251	+0.240

H9	+0.273	+0.237	+0.285
H10	+0.268	+0.237	+0.253
H11	+0.495	+0.442	+0.369
H12	+0.262	+0.227	+0.239
H21	+0.289	+0.277	+0.266
H31	+0.281	+0.263	+0.100
H61	+0.250	+0.206	+0.144
H71	+0.274	+0.245	+0.224
H41A	+0.283	+0.256	+0.207
H41B	+0.281	+0.251	+0.247
H41C	+0.276	+0.254	+0.246
H81A	+0.271	+0.235	+0.248
H81B	+0.274	+0.250	+0.218
H81C	+0.250	+0.218	+0.193
N1	-0.524	-0.522	-0.354
N2	-0.348	-0.392	+0.179
N3	-0.579	-0.508	-0.487
N4	-0.366	-0.394	+0.313
N11	-0.539	-0.540	-0.330
N21	-0.347	-0.392	+0.273
N31	-0.552	-0.493	-0.413
N41	-0.375	-0.376	+0.183
S1	+0.215	+0.176	-0.008
S2	+0.220	+0.141	+0.045
S11	+0.194	+0.147	+0.009
S21	+0.246	+0.177	+0.034

Polyiodides I_3^- and I_5^-

Figure S4. Polyiodide $[I_3]^-$: atom numbering scheme.

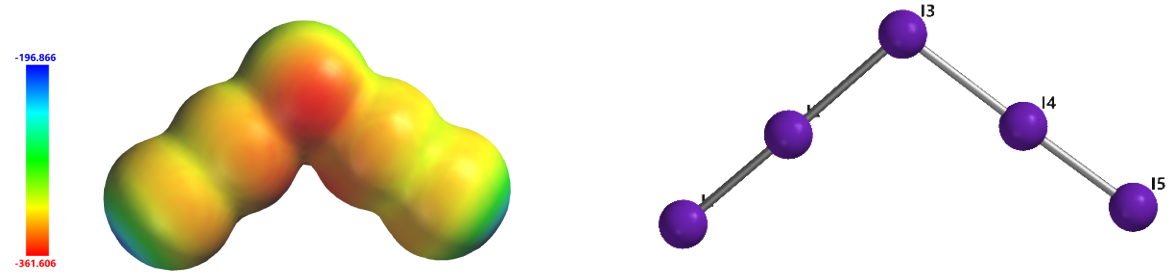

Figure S5. Polyiodide $[I_5]^-$: atom numbering scheme.

Table S5. Polyiodides $[I_3]^-$ and $[I_5]^-$: atomic charges (|e|).

Atom Label	Natural charge	Mulliken charge	Electrostatic charge
I1	-0.484	-0.491	-0.454
I2	-0.032	-0.017	-0.092
I3	-0.484	-0.491	-0.454

Atom Label	Natural charge	Mulliken charge	Electrostatic charge
I1	-0.311	-0.324	-0.288
I2	-0.007	+0.012	-0.085
I3	-0.374	-0.384	-0.266
I4	-0.006	+0.012	-0.078
I5	-0.303	-0.316	-0.283

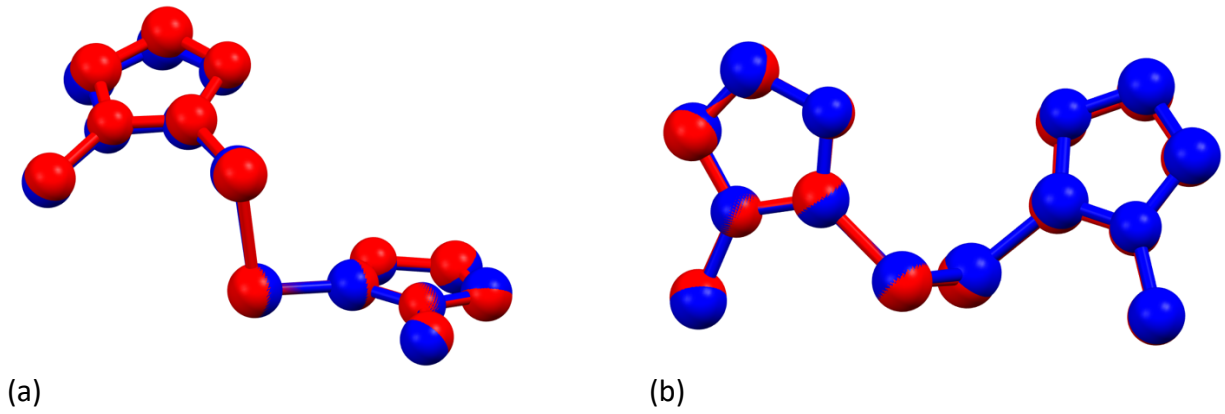

Figure S6. Side view (a) and front view (b) of the superposition of the crystal structures of the cations $[C_4H_5N_2S(11)\text{-}S(21)N_2C_4H_6]^+$ (**1-triclinic**, red) and $[C_4H_5N_2S(1)\text{-}S(4)N_2C_4H_6]^+$ (**1-monoclinic**, XIVBEJ, blue). H-atoms have been omitted for clarity.

Table S6. Solid state FT-Raman bands (450 – 50 cm^{-1}) of polymorphs **1-triclinic** and **1-monoclinic**, [**1** = $(C_4H_5N_2S\text{-}SN_2C_4H_6)_2I_3I_5$].

Compound	Polyiodide types	Bands (assignt.)[a]	I1-I2-I3[b] (Å)	I4-I5···I6···I7-I8[c] (Å)
1-triclinic	asymmetric I_3^-	112 (ν_1), 132 (ν_3)	I1-I2 2.9532 I2-I3 2.9019	
	V-shaped I_5^-: $I^- \rightarrow 2(I_2)$	160 [ν_1(I7-I8)], 172 [ν_1(I5-I4)]		I6-I5 3.113 I6-I7 3.020 I5-I4 2.7936 I7-I8 2.8255
1-monoclinic	symmetric I_3^-	113 (ν_1)	I1-I2 2.903 I2-I3 2.909	
	V-shaped I_5^-: $I^- \rightarrow 2(I_2)$	153 [ν_1(I7-I8)], 166 [ν_1(I5-I4)]		I6-I5 3.245 I6-I7 3.118 I5-I4 2.742 I7-I8 2.811

[a] (ν_1) symmetrical stretching, (ν_3) antisymmetrical stretching; [b] Angle I1-I2-I3: **1-triclinic** 178.98°, **1-monoclinic** 176.20°; [c] Angle I5-I6-I7: **1-triclinic** 96.35°, **1-monoclinic** 100.87°.

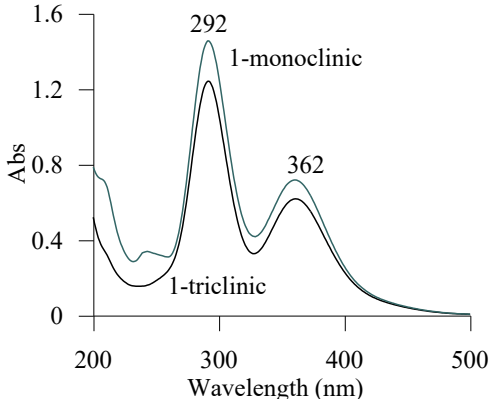

Figure S7. UV-Vis spectra of compound $[C_4H_5N_2S\text{-}SN_2C_4H_6]_2I_3I_5]$ in polymorphs **1-triclinic** and **1-monoclinic**. **1-triclinic** (CH_2Cl_2, T = 20 °C, M = 1.56 x 10^{-5}; λ =292 and 362 nm); **1-monoclinic (**CH_2Cl_2, T = 20 °C, M = 1.84 x 10^{-5}; λ =292 and 362 nm).