Electronic Supporting Information (ESI)

A new assembly of diiodine molecules at 1,3-Dimethylimidazole-2-thione (Me_2ImS) template: Crystal Structure of $(Me_2ImS)_2 \cdot (I_2)_5$

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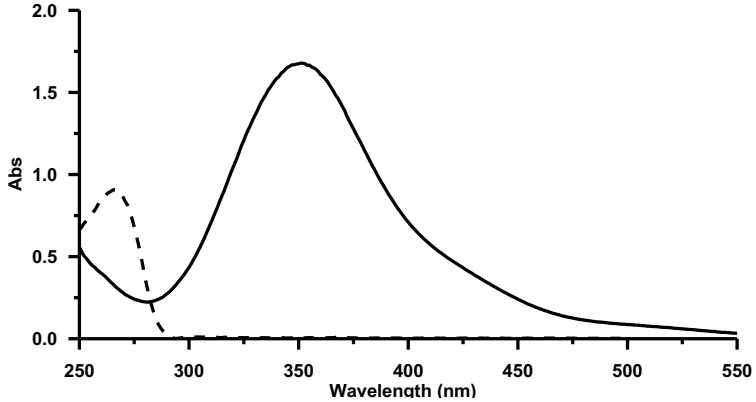


Figure S1. UV-Vis spectra: (—) compound (**1**) dissolved in CH_2Cl_2, [5.50 x 10^{-5} M], λ_{CT} = 350 nm (ε_{CT} = 30360 L mol^{-1} cm^{-1}); (···) Me_2ImS dissolved in CH_2Cl_2, [5.53 x 10^{-5} M]. *T* = 20°C.

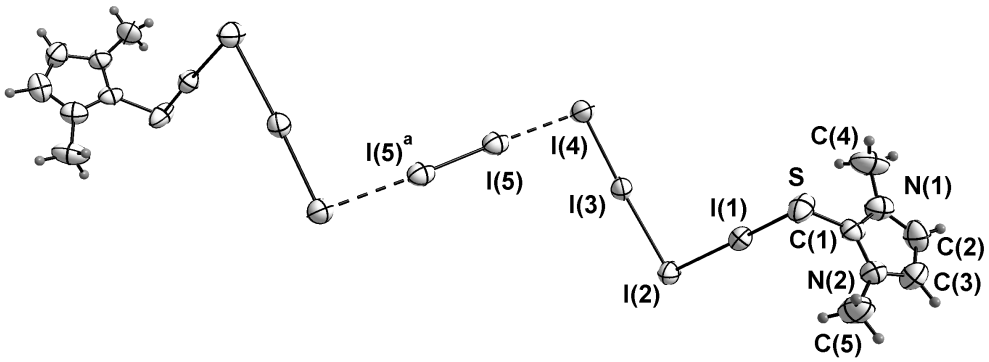


Figure S2. An ORTEP plot of $(Me_2ImS)_2 \cdot (I_2)_5$ with ellipsoids at 50% probability.

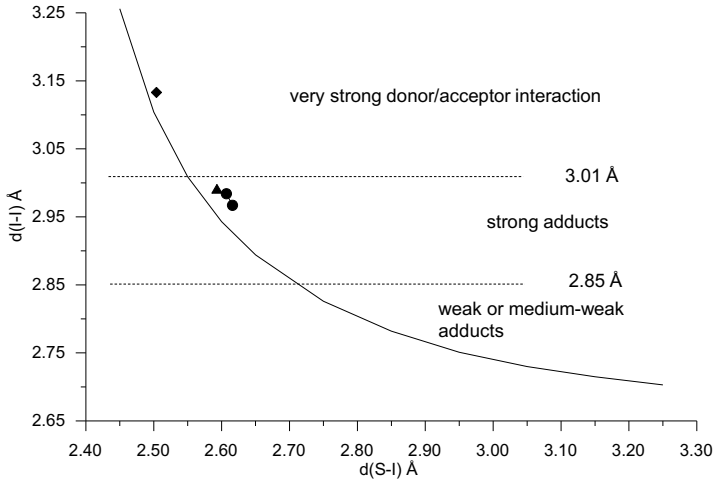


Figure S3. Dependence of the S-I *vs*. I-I bond distances proposed by Husebye[1] considering the structural data of 94 I_2-adducts with *S*-donors such as thioether, thiocarbonyl, and thioamide molecules. The curve was drawn considering the following equation

$$d(I–I) = d_0(I–I) – b(I–I)\ \ln\{1 – \exp[(d_0(S–I) – d(S–I))/b(S–I)]$$

where $d_0(I–I)$ = 2.67 Å [The I-I bond distance of I_2 in gas phase], $d_0(S–I)$ = 2.37 Å [the sum of Pauling's covalent radii], and b(I-I) = b(S-I) calculated to be 0.36.[1,2] In C.T. thione/thioamide-I_2 adducts having a S-I-I arrangement a direct relationship exists between the d(I-I) and d(S-I) bond distances from which the nature of the donor-acceptor interaction (very strong, strong, or weak adducts) can be classified.

Weak or medium-weak adducts: d(I-I) < 2.86 Å, the S···I_2 interaction can be seen as a perturbation induced by the *S*-donor on the diiodine molecule; strong adducts: 2.86 Å < d(I-I) < 3.01 Å, the molecular entity I-I can still be recognized and featuring, [S-I-I]; very strong adducts: d(I-I) > 3.01 Å.[3] Labels of adducts related to this article included in the graph: [$(Me_2ImS)_2(I_2)_5$] (♦); [$(Me_2ImS{\cdot}I_2(\alpha)$]: d(S-I1) 2.616 Å, d(I1-I2) 2.967 Å and [$(Me_2ImS{\cdot}I_2(\beta)$]: d(S-I1) 2.607 Å, d(I1-I2) 2.984 Å (●); [MeImHS·I_2] (▲).

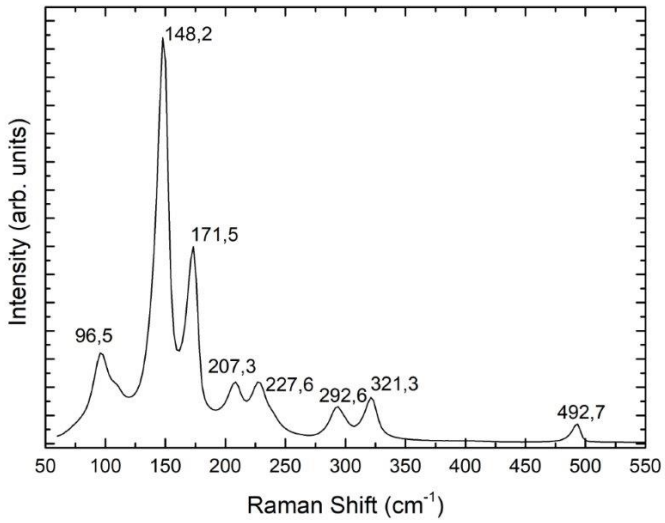


Figure S4. Raman spectrum of $(Me_2ImS)_2 \cdot (I_2)_5$.

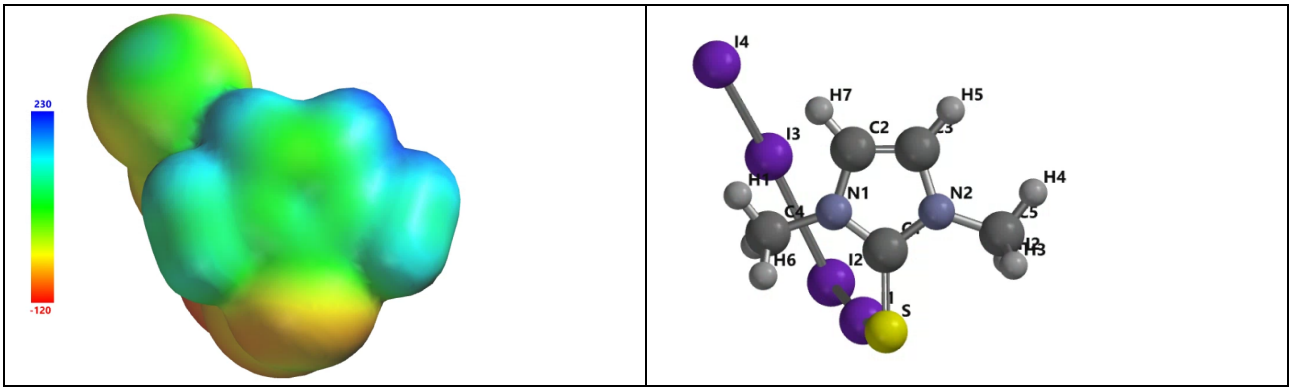


Figure S5. MEP map on the 0.002 a.u. isodensity surface of the fragment $[(Me_2ImS) \cdot (I_2) \cdot (I_2)]$ of compound (**1**). Color scale from -120 kJ/mol (red) to 200 kJ/mol (blue).

Table S1. Crystallographic data and structure refinement details

Compound	(**1**)
Formula	$C_5H_8I_5N_2S$
M.W.	762.69
Crystal system	triclinic
Space group	*P*-1 (no. 2)
a / Å	7.601(2)
b / Å	9.536(2)
c / Å	11.912(2)
α / º	101.98(2)
β / º	104.86(2)
γ / º	97.03(2)
V / Å^3	802.2(3)
Z	2
D_c /g/cm^{-3}	3.158
μ/ mm^{-1}	9.794
Measured reflections	2813
Unique reflections$_t$	2813,
Observed reflections [$I > 2\sigma(I)$]	2405
Parameters refined	119
Absorption correction	Psi-scan
θ_{min}, θ_{max}	0.499, 1.000
R	0.0284
*wR*2 [all data]	0.0841
GOF	1.124

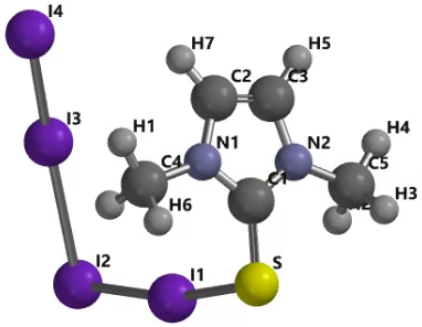
$R = \Sigma||Fo|-|Fc||/ \Sigma|Fo|$; $wR2 = \{ \Sigma[w(Fo^2-Fc^2)^2]/ \Sigma [w(Fo^2)^2]\}^{1/2}$;
$GOF = \{ \Sigma [w(Fo^2-Fc^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Table S2. Compound (**1**) - Selected interatomic distances (Å) and angles (deg.)

I(1)-I(2)	3.133(1)	I(1)-S	2.504(2)
I(2)-I(3)	3.076(1)	S-C(1)	1.732(7)
I(3)-I(4)	2.801(1)	N(1)-C(1)	1.320(9)
I(4) ···I(5)	3.447(1)	N(1)-C(2)	1.371(10)
I(5)···I(5)[a]	2.748(1)	N(1)-C(4)	1.453(10)
I(1) ···I(2)[c]	4.198(1)	N(2)-C(1)	1.343(8)
I(1)···I(4)[b]	4.200(2)	N(2)-C(3)	1.366(9)
I(4)···I(4)[d]	3.707(1)	N(2)-C(5)	1.449(10)
		C(2)-C(3)	1.331(11)
S-I(1)-I(2)	177.43(5)	I(1)-I(2)-I(3)	91.14(2)
I(2)-I(3)-I(4)	177.05(2)	C(1)-S-I(1)	100.1(2)
C(1)-N(1)-C(2)	108.9(6)	C(1)-N(1)-C(4)	125.4(7)
C(2)-N(1)-C(4)	125.7(8)	C(1)-N(2)-C(3)	108.2(6)
C(1)-N(2)-C(5)	126.3(6)	C(3)-N(2)-C(5)	125.5(7)
N(1)-C(1)-N(2)	107.9(6)	N(1)-C(1)-S	127.2(5)
N(2)-C(1)-S	124.8(5)	C(3)-C(2)-N(1)	107.3(7)
C(2)-C(3)-N(2)	107.7(7)		

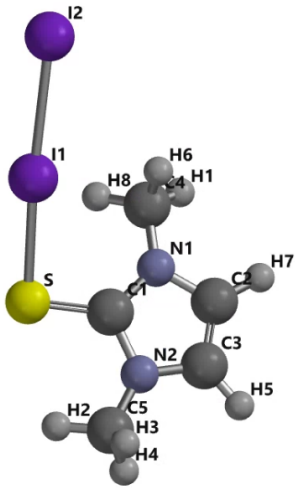
Symmetry codes: a = - x, -y-1,-z; b = x-1, y, z; c = -x, -y, 1-z; d = 1-x, -y, -z.

Table S3. $(Me_2ImS)\cdot(I_2)_2$ charges of atoms (|e|).



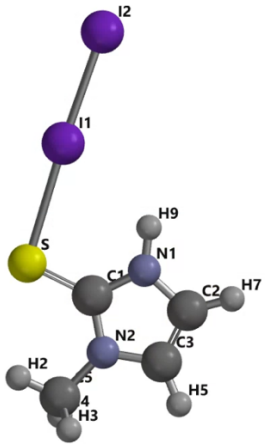
Atom label	Natural charge	Mulliken charge	Electrostatic charge
C1	+0.269	+0.317	-0.111
C2	-0.055	+0.01	-0.275
C3	-0.065	-0.01	-0.403
C4	-0.487	-0.373	-0.581
C5	-0.485	-0.37	-0.769
I1	+0.018	+0.021	-0.035
I2	-0.243	-0.249	-0.108
I3	+0.008	+0.018	-0.032
I4	-0.155	-0.162	-0.073
N1	-0.366	-0.41	+0.441
N2	-0.371	-0.415	+0.43
S	-0.173	-0.184	-0.195

Table S4. $Me_2ImS\cdot I_2(\alpha)$ charges of atoms (|e|).



Atom label	Natural charge	Mulliken charge	Electrostatic charge
C1	+0.271	+0.371	-0.124
C2	-0.074	-0.012	-0.396
C3	-0.079	-0.015	-0.258
C4	-0.483	-0.371	-0.729
C5	-0.498	-0.38	-0.633
I1	+0.009	+0.015	-0.050
I2	-0.153	-0.167	-0.091
N1	-0.393	-0.439	+0.503
N2	-0.393	-0.442	+0.303
S	-0.270	-0.293	-0.265

Table S5. MeImHS·I_2 charges of atoms (|e|).



Atom Label	Natural charge	Mulliken charge	Electrostatic charge
C1	+0.264	+0.368	-0.055
C2	-0.076	+0.002	-0.215
C3	-0.081	-0.011	-0.306
C4	-0.488	-0.380	-0.746
I1	-0.007	+0.008	-0.049
I2	-0.209	-0.219	-0.141
N1	-0.567	-0.606	-0.061
N2	-0.394	-0.434	+0.428
S	-0.208	-0.233	-0.233

References

1. M. D. Rudd, S. V. Lindeman, S. Husebye, *Acta Chem. Scan*., **1997**, 51, 689-708.
2. C. Ouvrard, J.-Y. Le Questel, M. Berthelot, C. Laurence, *Acta Crystallogr. B*, **2003**, 59(Pt 4), 512-526.
3. (*a*) V. Lippolis, F. Isaia, Handbook of Chalcogen Chemistry, Chapter 8.2, (Ed. F. A. Devillanova), RCS Publishing: Cambridge, U. K. 2007; pp. 477–496; (*b*) M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, G. Verani, *Dalton Trans.,* **2005**, 2252-2258, and references therein.