Electronic Supplementary Information for:

Novel Cyclen-Polyiodide Complexes: A Reappraisal of I-I Covalent and Secondary Bond Limits

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Table S1. Crystal data and refinement parameters for [(H_2Cyclen)·(I)·(I_3)] (**1**) and [(H_2Cyclen)$_2$.(I_5).(I_3)$_3$.(I_2)] (**2**).

	1	**2**
Empirical formula	$C_8H_{22}I_4N_4$	$C_{16}H_{44}I_{16}N_8$
Formula weight	681.89	2378.99
Temperature (K)	100	100
space group	*P2$_1$/c*	*P2$_1$/c*
a (Å)	9.5774(3)	16.587(1)
b (Å)	14.6567(5)	17.269(2)
c (Å)	13.1889(5)	17.219(2)
β (°)	94.860(1)	94.564(3)
Volume (Å^3)	1844.7(1)	4916.4(8)
Z	4	4
Independent reflections / R(int)	8943/0.0832	10080/0.0965
μ (mm^{-1})	6.745 (Mo-Kα)	10.093 (Mo-Kα)
R indices [I>2σ(I)]*	R1= 0.0432 wR2= 0.0942	R1= 0.0462 wR2= 0.0797
R indices (all data)*	R1= 0.0541 wR2= 0.0987	R1= 0.0784 wR2= 0.0924
CCDC no.		

* $R1 = \Sigma \, || Fo| - |Fc|| / \Sigma \, |Fo|$; $wR2 = = [\Sigma w(Fo^2 - Fc^2)^2 / \Sigma \, wFo^4]^{½}$

Table S2. Relevant distances in **1**. a) I-I bond distances in I_3^-, b) list of discussed short contacts in the crystal.

a)	Distance (Å)	Symmetry operation
I1-I2	2.9390(4)	
I2-I3	2.9078(4)	
b)		
I1···N4	3.794(3)	
I2···C1	3.960(4)	-x+1,-y+1,-z+1
I2···C2	3.974(4)	x+1,-y+1,-z+1
I2···C2	3.877(4)	-x+1,+y-½,-z+½
I3···N2	3.803(3)	-x+1,-y+1,-z+1
I4···N1	3.442(3)	
I4···N2	3.685(3)	-x+1,-y+1,-z+1
I4···N3	3.544(3)	x+1,+y,+z
I4···N3	3.645(3)	-x+1,-y+1,-z+1
C3···C6	3.742(6)	-x,+y+½,-z+½

Table S3. Relevant distances in **2**. a) I-I bond distances according to $[(H_2Cyclen)_2.(I_5).(I_3)_3.(I_2)]$ formula, b) list of discussed short contacts in the crystal (shorter to longer order), c) angles in polyiodides according to $[(H_2Cyclen)_2.(I_5).(I_3)_3.(I_2)]$ formula.

Contact	Distance (Å)	Symmetry operation
a)		
I1-I2	2.860(1)	
I2-I3	2.959(1)	
I4-I5	2.946(1)	
I5-I6	2.887(1)	
I7-I8	2.755(1)	
I9-I10	2.980(1)	
I10-I11	2.887(1)	
I12-I13	2.814(1)	
I13-I14	3.097(1)	
I14-I15	3.133(1)	
I15-I16	2.793(1)	
b)		
I8···I9	3.305(1)	
I6···I7	3.483(1)	
I3···N4	3.50(1)	
C16···C12	3.56(2)	x,-y+½+1,+z-½
C5···C1	3.59(2)	x,-y+½,+z+½
C1···I6	3.73(1)	
C9···I8	3.80(1)	
I1···I12	3.831(1)	x,-y+1/2+1,+z+½
C7···I11	3.84(1)	x,+y,+z+1
I4···I16	3.856(1)	-x+1,+y-½,-z+½
C9···I16	3.87(1)	x,-y+1/2+1,+z+½
C13···I10	3.88(1)	x,-y+½+1,+z+½
I2···I16	3.89(1)	x,-y+1/2+1,+z+1/2+1
I1···C14	3.90(1)	-x+1,+y-½,-z+½+1
I6···I7	3.901(1)	-x,-y+1,-z+1
C3···I6	3.92(1)	-x,+y-½,-z+½+1
I12···I1	3.945(1)	-x+1,+y+½,-z+½+1
C4···I15	3.95(1)	x,+y-1,+z+1
C7···I3	3.96(1)	-x,-y+1,-z+2
I4···C10	3.97(1)	-x+1,-y+1,-z+1

c)	
I1-I2-I3	178.58(4)°
I4-I5-I6	177.63(4)°
I9-I10-I11	173.78(3)°
I12-I13-I14	175.72(4)°
I13-I14-I15	121.86(4)°
I14-I15-I16	171.97(4)°

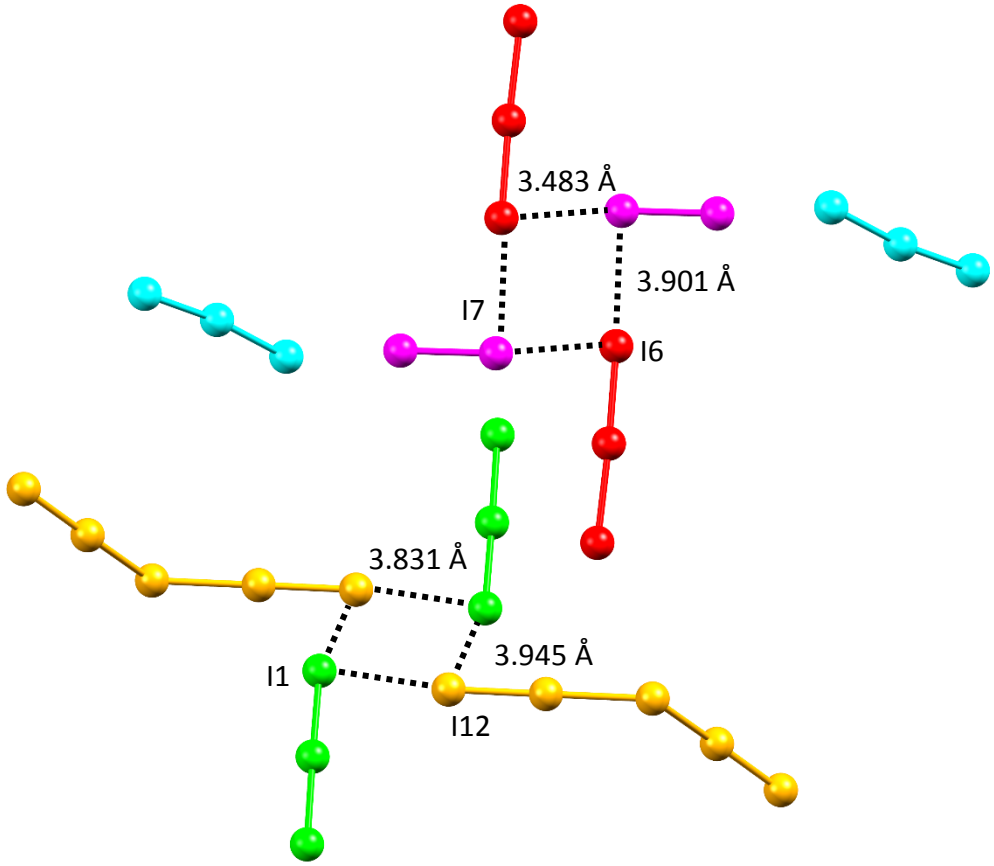

Figure S1. Details of I6···I7 and I1···I12 square-like contacts.

Notes on Employed CSD datasets

General and 1983 overall statistics

A generic I-single bond-I fragment with one of the two I atoms bearing a -1 charge was used to generate a dataset containing polyiodide crystal structures.

Upon it a search for I-I intramolecular distances was performed, specifying 0-4.5 Å range and a minimum and maximum number of covalent bonds in-between considered I atoms of 1 (i.e. direct I-I bonds). This constitutes the covalently bonded I-I fragments shown in the graphs.

A similar search was performed for contacts, i.e. searching on polyiodide dataset for I···I intermolecular contacts between 0 and 4.5 Å distance. This constitutes supramolecular I···I interactions as shown in the graphs.

A sum of covalent and supramolecular subsets was used to illustrate global data.

Searches were paired with a "before 1983" requirement through an AND function to reproduce available data in 1982.

Dataset for octaiodide, I_8^{2-}

Octaiodide search was performed by name ("octaiodide") to locate such structures where the anion was explicitly stated in the formula, since, when long bonds are involved, searches with fragments drawn as bonded might fail to locate all available material. This resulted in 35 hits, which have been manually discriminated as detailed below. A direct search for an I_8 fragment with 1-2-2-2-2-2-2-1 number of bonded atoms, corresponding to the most frequent $I_3^-\cdot I_2 \cdot I_3^-$ isomer, resulted in 28 hits, signifying that our search routine by compound name (35 hits) was mostly effective in gathering available data. A small number of crystal structures (red in the table below) was not comprised in our first search results and was then added. The reason is that some structures have been reported with "octa-iodide" spelling, thus eluding the "octaiodide" search but not the search by connectivity. A last entry, not included in any previous searches, was further included for consistency: DATRIZ01 (blue in the table below). This is because both DATRIZ and DATRIZ02 were located by above mentioned searches. While DATRIZ01 does not state "octaiodide" or "octa-iodide" in the formula, nor it formally contains a "bonded" I_8^{2-} unit (differently from isostructural DATRIZ and DATRIZ02): it appears as a good case in point about how much an organic revision of threshold bond distances might be required.

Octaiodide Dataset	
CSD Refcode	Notes
AZADPI	
AZADPI01	
BASHOS	Not used; no 3D coordinates available
BEVLAP	Not used; no 3D coordinates available
BUXPUF	Not used; no 3D coordinates available
BZHXDA	
BZHXDB	
CAZCUE	
CIMXIH	Not used; Disordered
CIYFOG	
DATRIZ	Not used; no 3D coordinates available
DATRIZ01	
DATRIZ02	
DIWQUV	
DOKBIO	Not used; it is an octa-iodide (8 I^-)
FIJWOK	Not used; no 3D coordinates available
GIXWIT	
GUGXAH	
GUHGOF	
HIJDUZ	
HILLOD	
HIPJAT	Not used; it is an octa-iodide (8 I^-)
JOJKID	Not used; it is an octa-iodide (8 I^-)
JOPLEH	
KOSFEF	Not used; it is an octa-iodide (8 I^-)
LOBKUI	Not used; an I_8 unit exists as P-bound moiety
MIWYIA	Not used; sole example of octaiodide with honeycomb structure
NABWUJ	
PACGOR	
PECXEB	Not used; it is an octa-iodide (8 I^-)
PECXEB01	Not used; it is an octa-iodide (8 I^-)
PONPAJ	
QAQSOQ	Not used; disordered
VAGKOE	
WEHQOS	Not used; it is an octa-iodide (8 I^-)
WITLIU	Contains 2 different octaiodides
XAGKAT	
XEHQIK	
YUPKEA	
YUPKIE	
ZEZDIR	