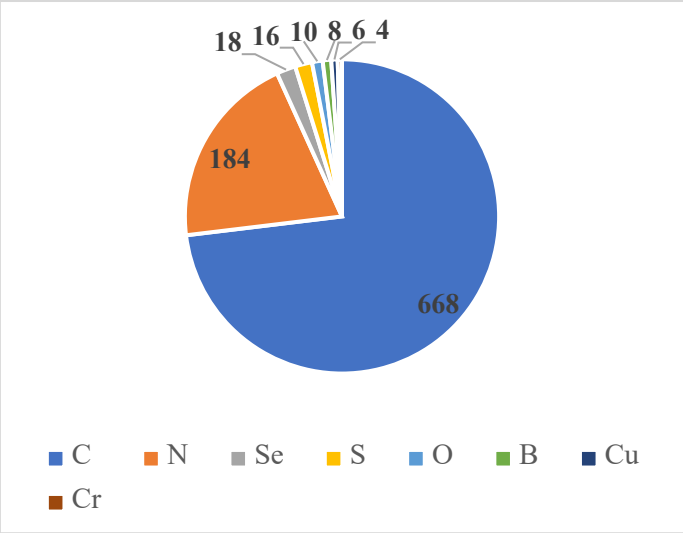
Arrangement of σ-Holes at Halogen Atom in Halonium Cation

Mariusz Michalczyk[1]*, and Wiktor Zierkiewicz[1]

[1]Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, email: mariusz.michalczyk@pwr.edu.pl

Table S1. The detailed results of the CSD survey.

$[D\cdots X\cdots D']^+$ angle	number of hits	Exemplary refcodes from CSD
30-40	1	WEVPOC
40-50	2	LEGVOL
50-60	0	
60-70	1	KELTEA
70-80	3	ISABUC, LOPQIQ
80-90	66	HIGVOL, ICIROE, ISACAJ, JOMMUW
90-100	283	AMEPAM, APUHIC, BEVVOR
100-110	32	HOHKAQ
110-120	0	
120-130	1	
130-140	1	
140-150	0	
150-160	0	
160-170	0	
170-180	88	EROFUP



C	668	73%
N	184	20%
Se	18	2%
S	16	2%
O	10	1%
B	8	1%
Cu	6	1%
Cr	4	0%

Figure S1. The distribution of the ligand atom connected to halogen atom within the CSD results.

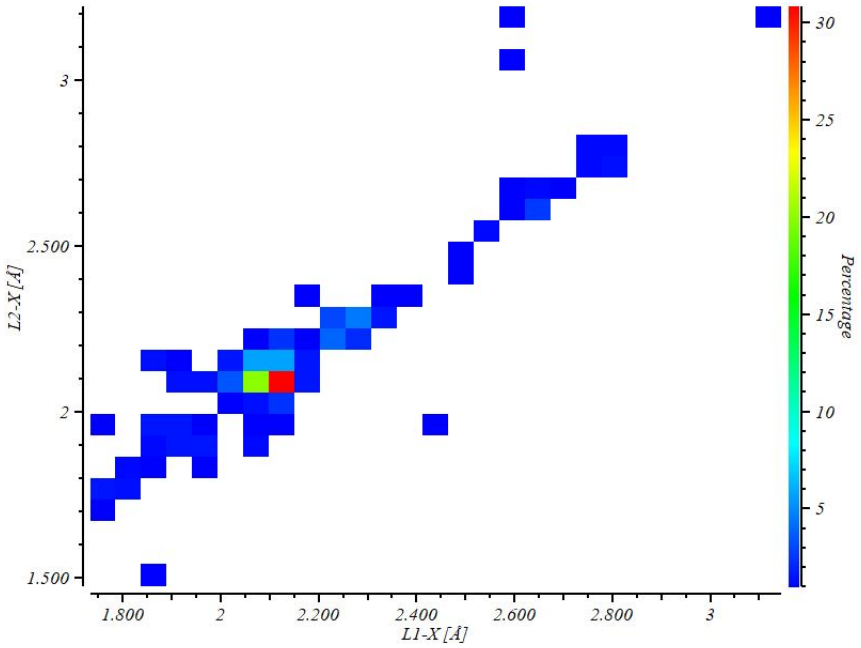


Figure S2. Heat plot representing the distribution of the L1-X and L2-X interatomic distances.

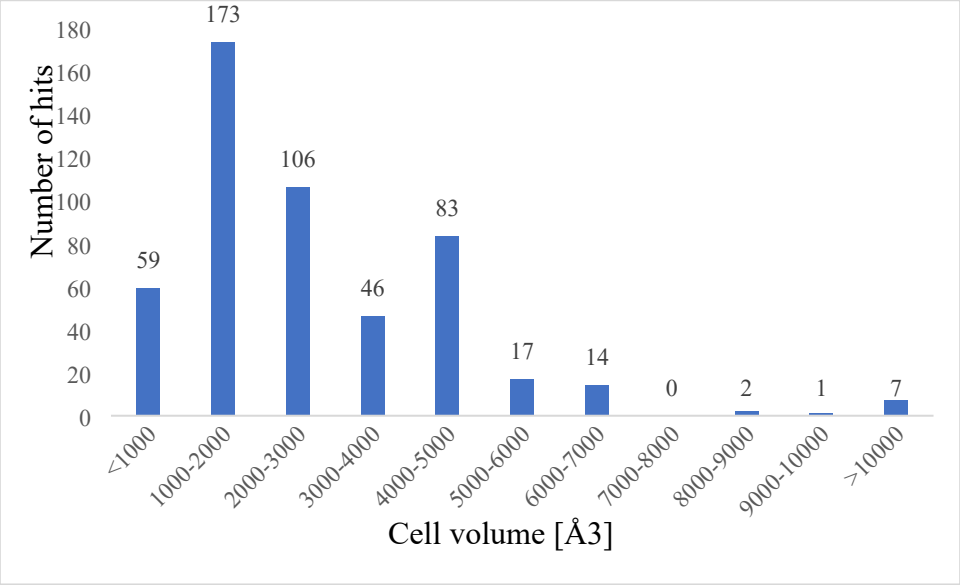


Figure S3. Distribution of the cell volumes across the CSD survey.

Table S2. Parameters for selected halonium cation monomers taken form the CSD survey. Structures which undergone detailed examination in the text are in bold font.

CSD Refcode	Halogen atom	∠L1-X-L2 [º]	Are ligands the same?	No of σ-holes	Vs,max [kcal/mol]
VEPXAQ	F	129.9	yes	2	106.7/107.5
NOCHUI	Cl	43.4	yes	1	83.2
LUSBUX	Cl	101.6	yes	2	140.2/140.2
NIXLUE	Cl	105.5	no	2	102.1/103.9
LEGVOL	Br	41.2	yes	1	87.7
AMEPAM	Br	91.1	no	2	101.7/118.5
HOHKAQ	Br	104.1	yes	2	134.8/134.9
WEVPOC	**I**	**36.0**	**yes**	**1**	**96.9**
ICIROE	I	93.6	yes	2	113.8/114.0
BEVVOR	**I**	**94.7**	**no**	**2**	**126.1/132.7**

Table S3. Geometrical parameters describing the σ-hole location of the $[H_5C_6\text{-}I\text{-}C_2F_2H]^+$model. Values for the equilibrium geometry are bolded. Potential in kcal/mol, angles in degrees.

Compound	α	β	Vmax(1)	Vmax(2)	∠C1XVmax(1)	∠C2XVmax(2)
$[H_5C_6\text{-}I\text{-}C_2F_2H]^+$	–	150.9	-	-	-	-
	92.4	140.9	105.8	107.7	154.2	154.6
	94.3	130.9	110.2	112.9	161.3	161.5
	99.5	120.9	114.4	117.8	168.9	169.2
	107.1	110.9	118.2	122.2	177.0	177.3
	111.4	**100.9**	**121.4**	**126.0**	**175.6**	**173.8**
	113.0	90.9	124.0	129.3	166.7	171.1
	115.5	80.9	125.8	131.4	165.9	159.4
	115.9	70.9	125.8	131.8	162.5	152.4
	105.6	60.9	120.9	128.3	174.1	141.1
	98.6	58.9	118.7	127.6	175.9	136.2
	94.0	56.9	116.0	127.1	167.2	130.1
	96.3	54.9	113.1	126.7	123.3	164.7
	97.2	52.9	110.1	126.3	117.6	162.1
	-[a]	50.9	125.8[a]		161.4	147.7[b]

[a] only one σ-hole exists

[b] ∠C2XVmax(1)

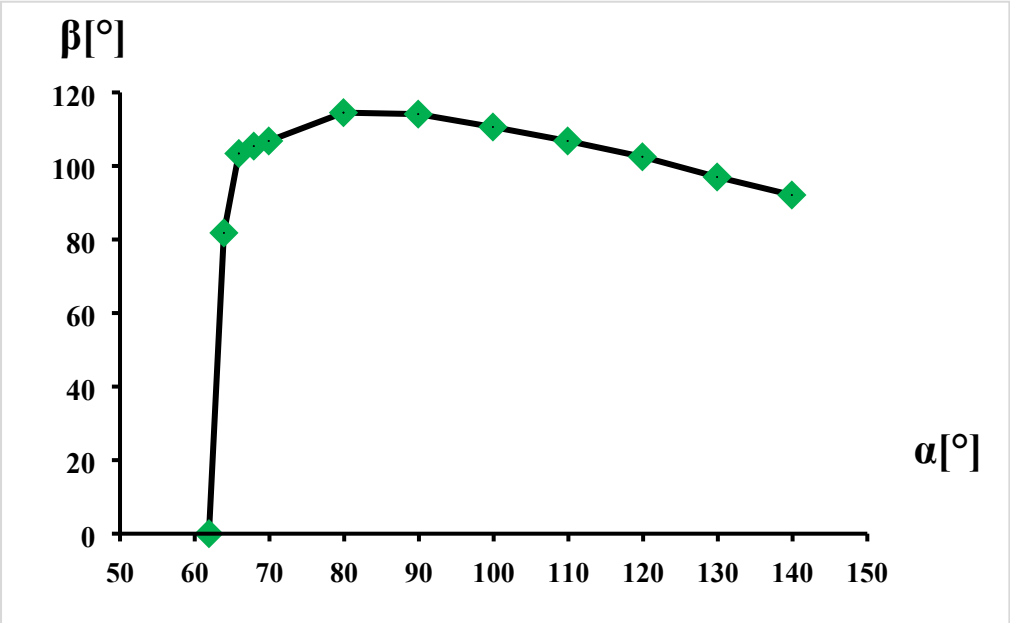


Figure S4. Chart representing changes of β angle versus α angle in the $[H_5C_6\text{-}I\text{-}C_2F_2H]^+$model.

Table S4. Geometrical parameters describing the σ-hole location of the $[H_5C_6\text{-}I\text{-}C_5H_6]^+$ model. Values for the equilibrium geometry are bolded. Potential in kcal/mol, angles in degrees.

Compound	α	β	Vmax(1)	Vmax(2)	∠C1XVmax(1)	∠C2XVmax(2)

$[H_5C_6\text{-}I\text{-}C_5H_6]^+$	-	159.9	-	-	-	-
	89.3	149.9	91.3	91.3	148.3	148.2
	92.1	139.9	96.1	96.1	156.3	155.6
	97.0	129.9	100.7	100.7	163.9	163.2
	102.5	119.9	104.9	104.9	170.5	171.7
	106.8	109.9	108.7	108.6	178.4	177.6
	110.6	**99.9**	**111.8**	**111.8**	**173.7**	**175.4**
	114.1	89.9	114.0	114.0	167.7	167.9
	114.5	79.9	115.2	115.2	163.6	161.7
	106.8	69.9	114.8	114.9	162.2	160.9
	105.4	67.9	114.5	114.5	162.1	160.4
	103.4	65.9	114.0	114.0	161.4	161.0
	81.8	63.9	113.5	113.5	171.1	170.9
	-[a]	61.9	113.8[a]		148.8	149.3[b]

[a] only one σ-hole exists

[b] ∠C2XVmax(1)

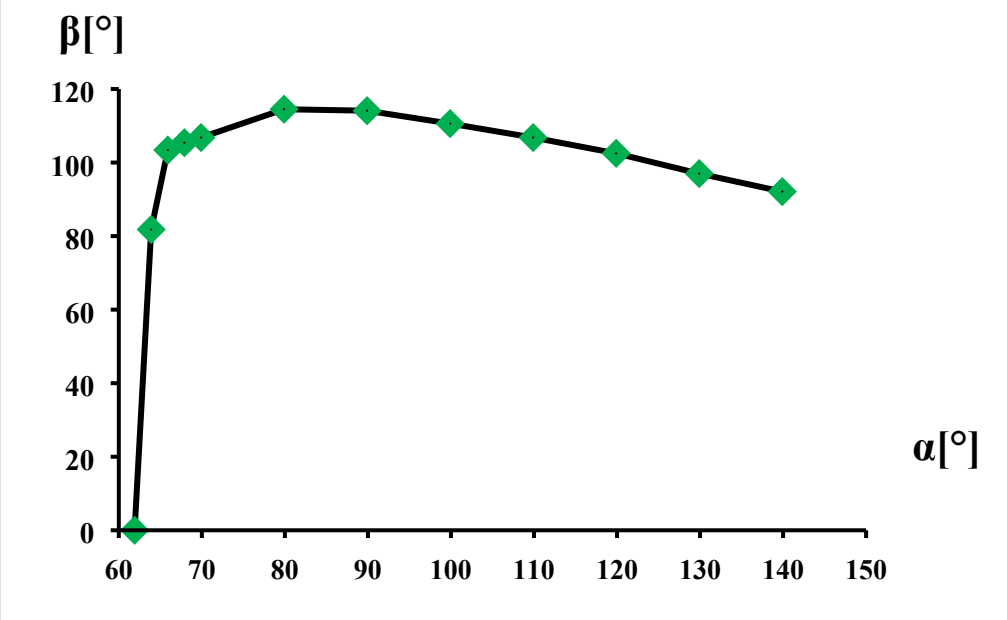


Figure S5. Chart representing changes of β angle versus α angle in the $[H_5C_6\text{-}I\text{-}C_5H_6]^+$ model.

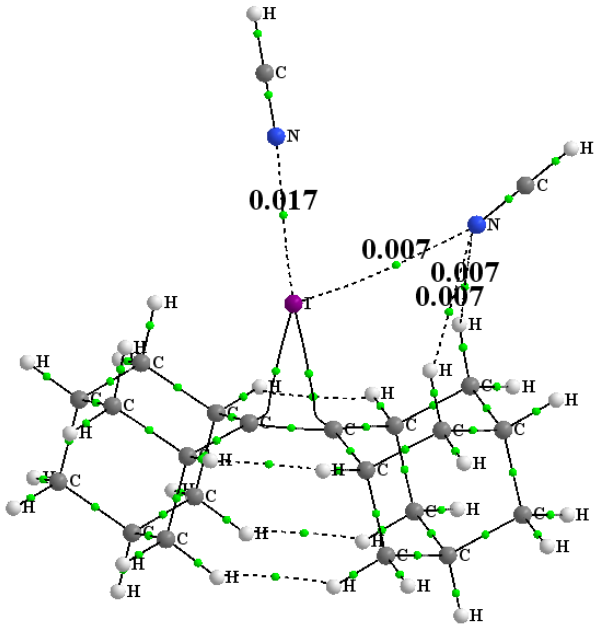


Figure S6. The QTAIM molecular diagram for the WEVPOC crystal structure with two HCN ligands. Values at BCPs (green dots) are the electron density (ρ) given in au.

Table S5. Coordinates of the DFT optimized halonium cation models.

Compound	Coords			
HF_2C_2-Cl-C_2F_2H	F	6.52365900	5.78899400	12.34066700
	F	7.94898400	4.20328500	12.56010700
	C	7.53005800	5.57267500	14.38615900
	H	7.02786200	6.39003300	14.87320600
	C	7.34221200	5.19014000	13.12341000
	C	10.17213800	5.40334900	15.31016200
	H	10.82392700	5.14236400	14.49496700
	C	10.47894100	6.22316300	16.31511600
	F	9.68629000	6.51775400	17.28686300
	F	11.61660300	6.80603300	16.40080900
	Cl	8.61997100	4.63302500	15.35227600
HF_2C_2-Br-C_2F_2H	F	6.51086100	5.84634700	12.29255300
	F	7.90906900	4.23776500	12.49884700
	C	7.44581400	5.54742400	14.36306300
	H	6.92919200	6.35668600	14.84830800
	C	7.29665900	5.21092500	13.08358500
	C	10.24567900	5.37892100	15.36213400

	H	10.91050600	5.10969600	14.56040200
	C	10.53509300	6.24820400	16.32807100
	F	9.74353600	6.56984400	17.29451500
	F	11.65863500	6.86590400	16.38347200
	Br	8.58560100	4.49909700	15.42879100
HF_2C_2-I-C_2F_2H	I	8.54445000	4.35762900	15.51596200
	F	6.48003000	5.89244000	12.22931600
	F	7.85319100	4.26608800	12.42643900
	C	7.34566700	5.51832600	14.32432000
	H	6.80601800	6.32719900	14.78613200
	C	7.23338100	5.22654600	13.03062200
	C	10.32890600	5.36380800	15.42742900
	H	11.01529700	5.10574600	14.63933500
	C	10.61222700	6.27341800	16.35681900
	F	9.82929300	6.61774600	17.32645800
	F	11.72218500	6.92186800	16.38090900
H_5C_6-Cl-C_2F_2H	F	6.23486700	5.82743600	12.72836900
	F	8.34091000	6.11014300	13.02018600
	C	8.71736600	5.88182200	16.74366800
	C	9.33120800	7.06353600	16.38133400
	H	9.72992400	7.22018100	15.38906100
	C	9.41965600	8.03782300	17.36562600
	H	9.89326300	8.98143000	17.13494000
	C	8.91199400	7.79736000	18.63704300
	H	8.99078400	8.56399400	19.39508200
	C	8.31094300	6.58475900	18.95045500
	H	7.92510700	6.40536300	19.94384400
	C	8.20390200	5.58808800	17.98970700
	H	7.74782000	4.63355400	18.21013000
	C	7.16241800	4.88238600	14.60007700
	H	6.25651900	4.44752000	14.98328500
	C	7.25089600	5.58945200	13.47753000
	Cl	8.61582200	4.59755200	15.49476300
H_5C_6-Br-C_2F_2H	F	6.14155400	5.87132100	12.74169000
	F	8.24142500	6.19744900	13.01866600
	C	8.78379700	5.87412100	16.78234100
	C	9.40416900	7.05498400	16.42410500
	H	9.83872900	7.20075400	15.44554900
	C	9.45016600	8.04918600	17.39199500
	H	9.92689400	8.99097100	17.15977100
	C	8.89545000	7.83166300	18.64713800
	H	8.94117700	8.61326000	19.39249700
	C	8.28836100	6.62200800	18.95970900

	H	7.86421100	6.45938500	19.94040900
	C	8.22368300	5.60590500	18.01544000
	H	7.76166500	4.65589000	18.24191000
	C	7.13338200	4.80282500	14.51376300
	H	6.24208700	4.31575900	14.86699800
	C	7.17889200	5.60156600	13.45356600
	Br	8.72775700	4.46535200	15.44955400
H_5C_6-I-C_2F_2H	I	8.81557200	4.30475800	15.41573200
	F	6.07110500	5.92183100	12.70892800
	F	8.16825900	6.23925500	12.99055600
	C	8.84306200	5.85761300	16.83521500
	C	9.45418200	7.04769900	16.47525800
	H	9.90718700	7.18755900	15.50404100
	C	9.46755700	8.06431700	17.42010100
	H	9.93547100	9.00760300	17.17579300
	C	8.89059900	7.86821000	18.66835800
	H	8.91016900	8.66671300	19.39686400
	C	8.29303900	6.65746700	18.99361300
	H	7.84943900	6.51041400	19.96827600
	C	8.26156700	5.62178900	18.06983800
	H	7.80167900	4.67522600	18.31476600
	C	7.08253400	4.73714700	14.40208800
	H	6.17846500	4.24017400	14.70811200
	C	7.11351300	5.60462500	13.39756200
H_5C_6-Cl-C_6H_5	C	1.69783500	5.51809400	3.48662700
	C	0.91373800	6.21618800	4.38115900
	C	0.24823900	7.33146400	3.88807800
	C	0.38381500	7.69347000	2.55491400
	C	1.18748600	6.95558300	1.69309100
	C	1.87133700	5.84158400	2.15651100
	H	0.82802400	5.91566900	5.41561800
	H	-0.37493000	7.91281900	4.55255100
	H	-0.13963100	8.56264900	2.18219500
	H	1.29096600	7.24817200	0.65792500
	H	2.50764800	5.25580000	1.50837500
	C	1.76995000	2.67594200	3.40529700
	C	0.51745200	2.33976400	3.87674500
	C	2.46727500	1.98774700	2.43432500
	C	-0.08042200	1.22280000	3.31226600
	H	0.02699800	2.91793900	4.64698600
	C	1.84457300	0.86964800	1.89411300
	H	3.45226200	2.29787100	2.11593100
	C	0.58093400	0.49485900	2.32948900

	H	-1.06183100	0.92021900	3.64867300
	H	2.35391900	0.29606200	1.13292000
	H	0.10582500	-0.37665600	1.90152200
	Cl	2.57713500	4.09881500	4.12129200
H_5C_6-Br-C_6H_5	C	1.78809300	5.60292400	3.43972100
	C	0.56412100	5.96624100	3.96560300
	C	-0.07444300	7.04795600	3.37566000
	C	0.51926500	7.71880600	2.31337600
	C	1.75568700	7.32141800	1.82332100
	C	2.41777300	6.23875000	2.38838800
	H	0.12186600	5.43746800	4.79770000
	H	-1.03491000	7.36671100	3.75518200
	H	0.01356200	8.56289600	1.86590400
	H	2.21384400	7.85039000	0.99969200
	H	3.38254200	5.91744800	2.02320000
	C	1.73755500	2.59311400	3.51239700
	C	0.86374300	1.93730300	4.35628100
	C	1.97964000	2.24559700	2.19816500
	C	0.18018900	0.84921500	3.82822700
	H	0.71956700	2.24800100	5.38096500
	C	1.27635200	1.15876600	1.69837000
	H	2.68332700	2.79012000	1.58504300
	C	0.38499300	0.46707500	2.50965300
	H	-0.51148900	0.30444200	4.45503100
	H	1.43409200	0.85201900	0.67408500
	H	-0.15272800	-0.38106500	2.10971400
	Br	2.70596000	4.10090400	4.24092000
H_5C_6-I-C_6H_5	I	2.83429200	4.09199900	4.36231200
	C	1.77617900	5.70366300	3.52096100
	C	0.76909800	6.28383800	4.27345800
	C	0.07744600	7.34548800	3.70570200
	C	0.39953400	7.78887400	2.43017000
	C	1.41735800	7.18277300	1.70518900
	C	2.12916800	6.12314600	2.24949200
	H	0.52639300	5.93403800	5.26662300
	H	-0.71294400	7.82331900	4.26737100
	H	-0.14494200	8.61665000	1.99820400
	H	1.66671200	7.53467600	0.71397400
	H	2.92853100	5.65156400	1.69592500
	C	1.79889900	2.48399700	3.48662600
	C	0.65436100	2.02261800	4.11469500
	C	2.30575700	1.94853200	2.31460500
	C	-0.01946400	0.96546200	3.51870100
	H	0.29376300	2.45983500	5.03486300

	C	1.61184500	0.89142400	1.74170300
	H	3.20867700	2.32852400	1.85855700
	C	0.45724700	0.40580500	2.34040200
	H	-0.91628800	0.57993300	3.98316800
	H	1.98098900	0.44939400	0.82696600
	H	-0.07401200	-0.41905200	1.88693700
H_5C_6-Cl-C_6F_5	Cl	2.56584600	4.09522600	4.11886500
	C	1.72786200	5.53153100	3.44068600
	C	0.67495000	6.04447300	4.16997100
	C	0.05342900	7.16705700	3.64028800
	C	0.49774500	7.71449100	2.44268900
	C	1.56782200	7.15746800	1.75274000
	C	2.21433800	6.03517200	2.25194500
	H	0.35553600	5.60059400	5.10215200
	H	-0.77553500	7.61238400	4.17166900
	H	0.00534700	8.59004400	2.04326500
	H	1.90880300	7.59531200	0.82543000
	H	3.05337400	5.58453700	1.74123500
	C	1.75037600	2.70912400	3.46533300
	C	0.68642800	2.15748100	4.16667900
	C	2.19119900	2.16907400	2.26446100
	C	0.05629700	1.03581100	3.66006200
	F	0.28258400	2.69953300	5.29645200
	C	1.55934200	1.04802900	1.75884700
	F	3.19477000	2.72158800	1.61559400
	C	0.49638500	0.48723500	2.45974000
	F	-0.95142300	0.49395000	4.30281500
	F	1.95516400	0.51766800	0.62574900
	F	-0.10203700	-0.57128100	1.97993200
H_5C_6-Br-C_6F_5	Br	2.70079500	4.10027100	4.23771000
	C	1.76027000	5.61369800	3.46737800
	C	0.68298700	6.11239300	4.17244600
	C	0.03070200	7.20207300	3.61093100
	C	0.46811500	7.73629900	2.40523500
	C	1.56117100	7.19690300	1.73851400
	C	2.23825700	6.10719300	2.26976900
	H	0.36329600	5.68345000	5.11134400
	H	-0.81792700	7.63137800	4.12443600
	H	-0.04788900	8.58632100	1.98121600
	H	1.89653000	7.62205100	0.80313500
	H	3.09319600	5.67387800	1.77083200
	C	1.78044400	2.62757800	3.49886300
	C	0.71430100	2.07402400	4.19393300

	C	2.19147300	2.11491800	2.27636200
	C	0.05292500	0.98233100	3.66101500
	F	0.32959300	2.58359700	5.34708100
	C	1.52982200	1.02407800	1.74274000
	F	3.19732700	2.66394300	1.62445700
	C	0.46473700	0.46240900	2.43872500
	F	-0.95875700	0.44211600	4.30036100
	F	1.89968400	0.52316000	0.58667400
	F	-0.16245200	-0.56756200	1.93344300
H_5C_6-I-C_6F_5	I	2.88683400	4.10787900	4.30949800
	C	1.80454500	5.71161700	3.48344400
	C	0.72530500	6.19806500	4.20230600
	C	0.02117800	7.25628900	3.64439600
	C	0.40614900	7.78562600	2.41927300
	C	1.49694600	7.26960500	1.73122400
	C	2.22239400	6.21142900	2.26123200
	H	0.43658000	5.77848500	5.15542400
	H	-0.82740300	7.66487900	4.17481800
	H	-0.14892400	8.61157400	1.99682400
	H	1.79185500	7.68870900	0.77951000
	H	3.07410400	5.80269800	1.73635100
	C	1.83515100	2.52606300	3.49376700
	C	0.70814800	2.04269600	4.14491400
	C	2.25959400	1.95838800	2.29997000
	C	0.00430600	0.98113200	3.60665200
	F	0.29657100	2.59441200	5.27239900
	C	1.56048900	0.89561900	1.75687700
	F	3.32333700	2.42768400	1.67378600
	C	0.43563200	0.41105400	2.41422000
	F	-1.06537200	0.51527300	4.21116800
	F	1.95051300	0.34923800	0.62729600
	F	-0.22933100	-0.59191600	1.90125200