Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Multi-Center Covalency: Revisiting the Nature of Anion-π Interactions

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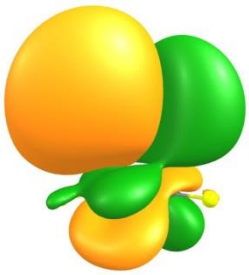
Figure S1. Bonding molecular orbitals of sample stable complexes, 5Cl(π), and 8Cl(π). The isosurfaces values at which the MO is visualized is presented in atomic units.

5Cl(π)

HOMO

5Cl(π)

Iso: 0.0058



HOMO-1

5Cl(π)

Iso: 0.0018

HOMO-3

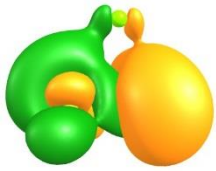
5Cl(π)

Iso: 0.0026

HOMO-4

5Cl(π)

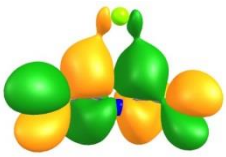
Iso: 0.0060



HOMO-5

5Cl(π)

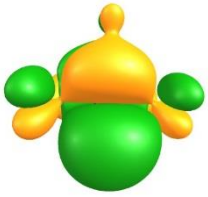
Iso: 0.0060



HOMO-6

5Cl(π)

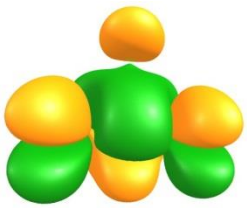
Iso: 0.0100



HOMO-7

5Cl(π)

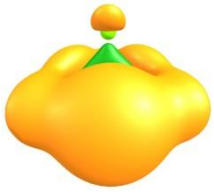
Iso: 0.0100



HOMO-8

5Cl(π)

Iso: 0.0040



HOMO-9

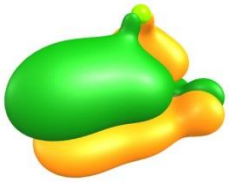
5Cl(π)

Iso: 0.0020

HOMO-13

5Cl(π)

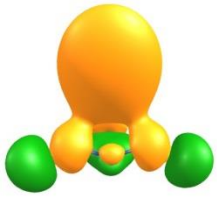
Iso: 0.0025



HOMO-14

5Cl(π)

Iso: 0.0025



HOMO-19

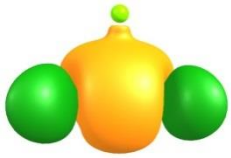
5Cl(π)

Iso: 0.0100

HOMO-20

5Cl(π)

Iso: 0.0120

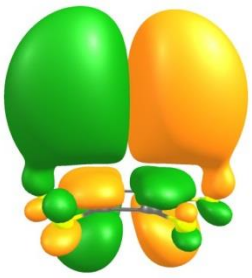


HOMO-25

5Cl(π)

Iso: 0.0025

8Cl(π)



HOMO

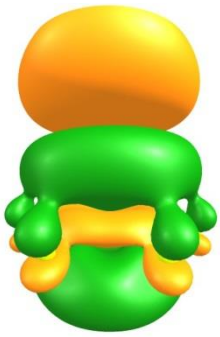
8Cl(π)

Iso: 0.0035

HOMO-1

8Cl(π)

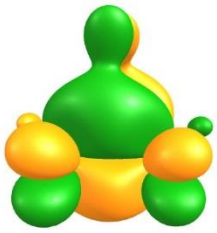
Iso: 0.0035



HOMO-2

8Cl(π)

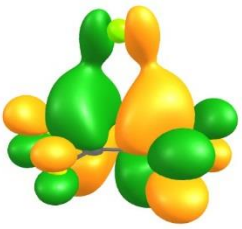
Iso: 0.0035



HOMO-3

8Cl(π)

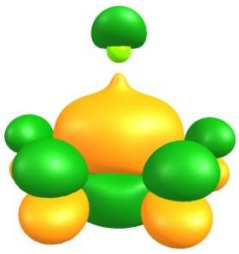
Iso: 0.0150



HOMO-4

8Cl(π)

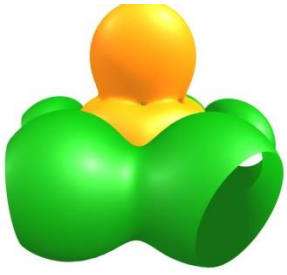
Iso: 0.0150



HOMO-5

8Cl(π)

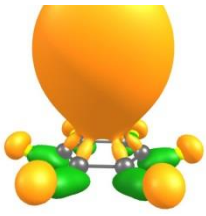
Iso: 0.0150



HOMO-23

8Cl(π)

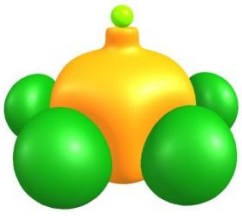
Iso: 0.0012



HOMO-25

8Cl(π)

Iso: 0.0080

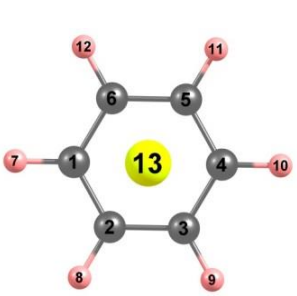


HOMO-30

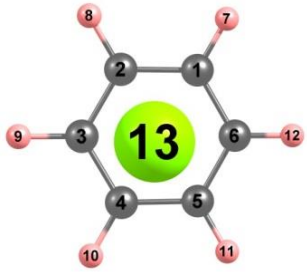
8Cl(π)

Iso: 0.0030

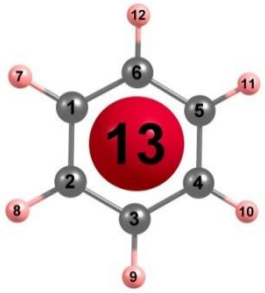
Figure S2. Structures of all studied species with atom numbering; the numbers are useful for understanding Table S1.



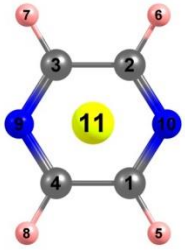
1F(π)



1Cl((π)

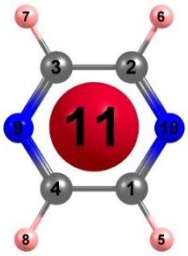


1Br(π)

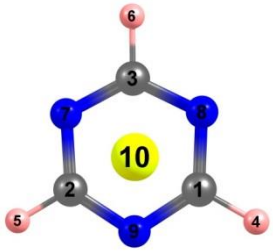


2F(π)

2Cl(π)

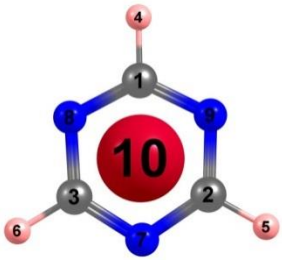


2Br(π)

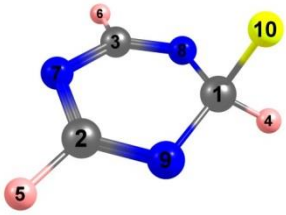


3F(π)

3Cl(π)



3Br(π)

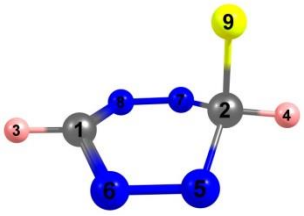


3F(σ)

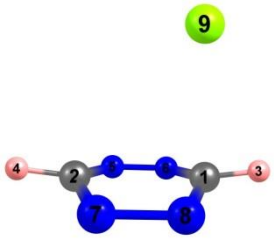
4F(π)

4Cl(π)

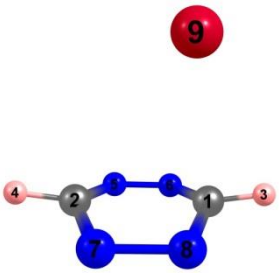
4Br(π)



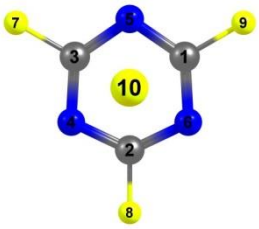
4F(σ)



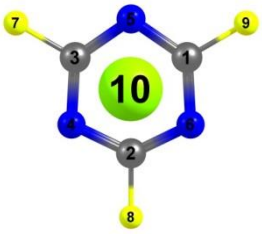
4Cl(σ)



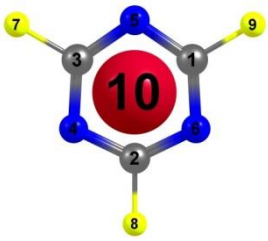
4Br(σ)



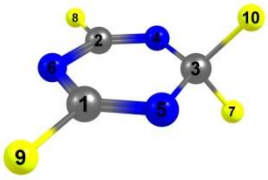
5F(π)



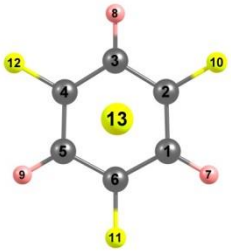
5Cl(π)



5Br(π)

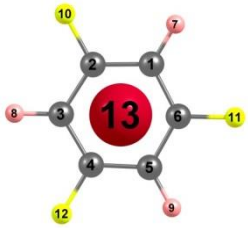


5F(σ)



6F(π)

6Cl(π)



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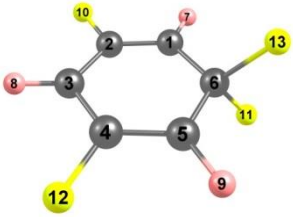
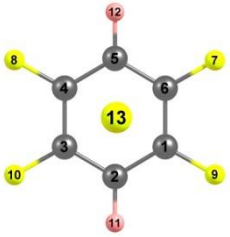


6F(σ)



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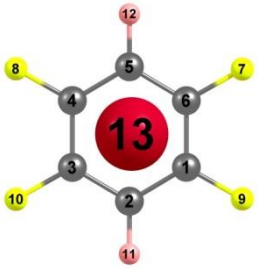

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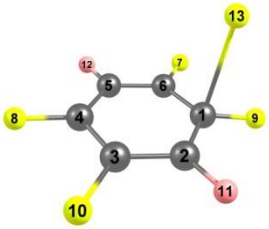

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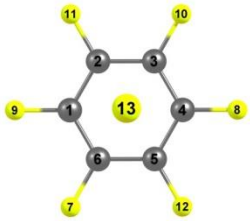
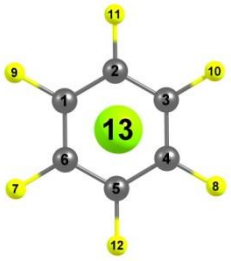
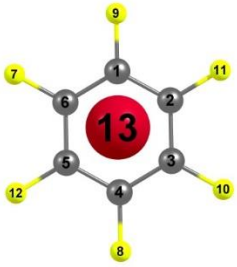


8F(π)



8Cl(π)



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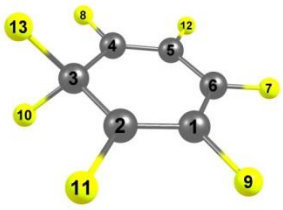
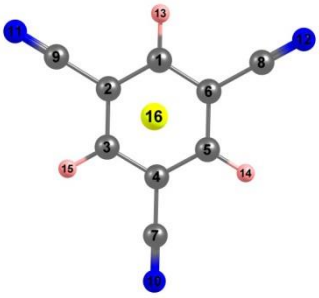
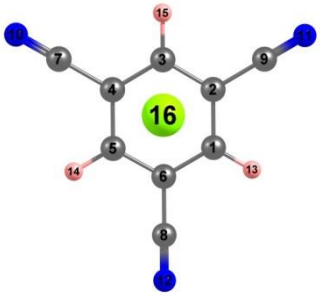


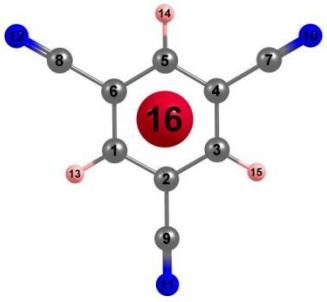
8F(σ)



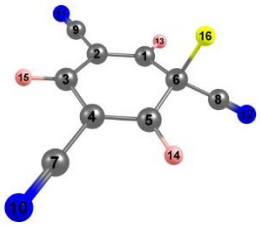
9F(π)



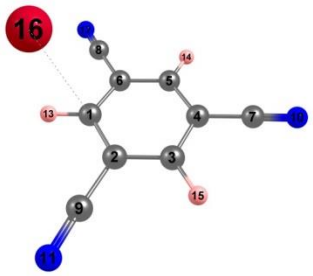
9Cl(π)



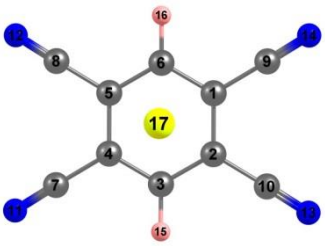
9Br(π)



9F(σ)



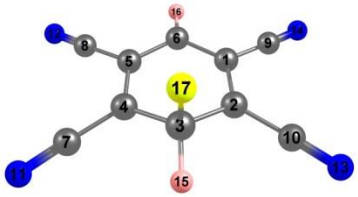
9Br(σ)



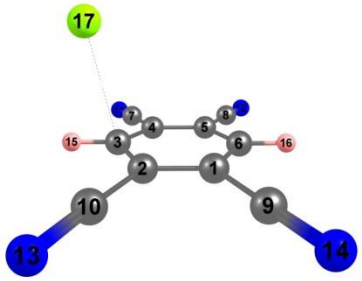
10F(π)

10Cl(π)

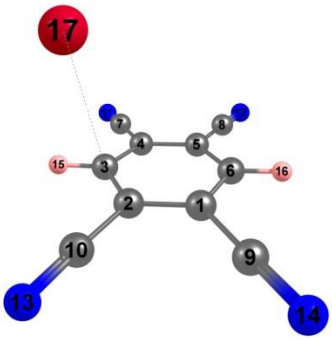
10Br(π)



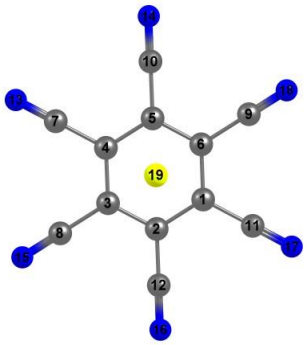
10F(σ)



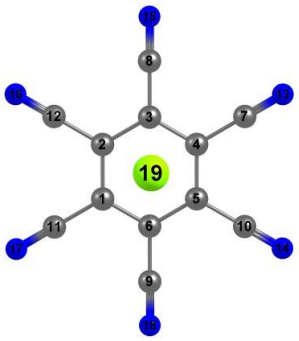
10Cl(σ)



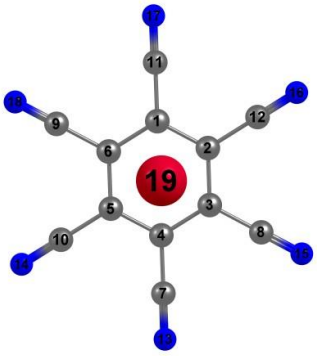
10Br(σ)



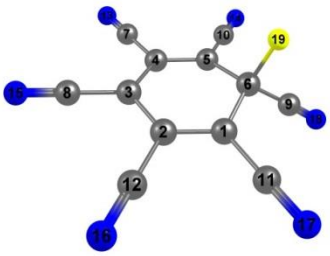
11F(π)



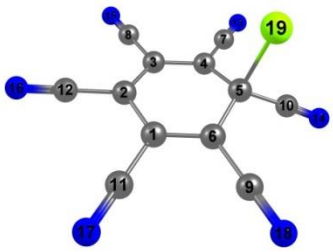
11Cl(π)



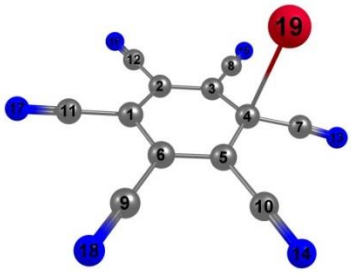
11Br(π)



11F(σ)



11Cl(σ)



11Br(σ)

Table S1. Delocalization index, exchange-correlation potential and electrostatic potential between halides and all atoms in the complexes. For numbering see Figure S2.

Complex	Atom No.	δ(X,Ω)	V_{XC}(X,Ω)	V_{El}(X,Ω)	Complex	Atom No.	δ(X,Ω)	V_{XC}(X,Ω)	V_{El}(X,Ω)
1f(π)	X-C	0.029	-10.8	-9.2	9f(π)	X-C1/3/5	0.050	-22.1	-54.8
	X-H	0.001	-0.3	5.7		X-C2/4/6	0.052	-22.7	-50.3
1cl(π)	X-C	0.026	-8.3	-2.7		X-C7/8/9	0.006	-1.4	-309.2
	X-H	0.002	-0.4	2.6		X-N10/11/12	0.003	-0.5	376.4
1br(π)	X-C	0.027	-8.3	-1.7		X-H	0.002	-0.4	-22.9
	X-H	0.002	-0.4	2.2	9cl(π)	X-C1/3/5	0.046	-17.3	-34.3
2f(π)	X-C	0.040	-17.3	-274.3		X-C2/4/6	0.049	-18.3	-34.5
	X-N	0.050	-19.0	515.6		X-C7/8/9	0.007	-1.8	-280.4
	X-H	0.002	-0.5	0.2		X-N10/11/12	0.003	-0.6	339.1
2cl(π)	X-C	0.036	-13.1	-214.2		X-H	0.002	-0.5	-22.1
	X-N	0.044	-14.1	425.8	9br(π)	X-C1/3/5	0.045	-16.3	-30.3
	X-H	0.003	-0.6	-3.2		X-C2/4/6	0.048	-17.3	-31.2
2br(π)	X-C	0.036	-12.4	-200.9		X-C7/8/9	0.008	-2.0	-271.5
	X-N	0.043	-13.4	403.9		X-N10/11/12	0.004	-0.7	327.9
	X-H	0.003	-0.7	-3.8		X-H	0.003	-0.6	-21.6
3f(π)	X-C	0.033	-14.7	-565.2				0.0	0.0
	X-N	0.062	-25.9	542.6	9f(σ)	X-C6	0.654	-495.5	-427.5
	X-H	0.002	-0.6	-6.8		X-C1/5	0.115	-44.0	-12.1
3f(σ)	X-C1	0.644	-503.8	-924.4		X-C2/4	0.020	-4.7	-14.5
	X-C2/3	0.019	-4.7	-388.2		X-C3	0.031	-5.6	-5.2
	X-N8/9	0.149	-66.8	475.8		X-C8	0.112	-55.8	-342.0
	X-N7	0.024	-5.1	345.3		X-N12	0.034	-8.6	398.1
	X-H4	0.077	-33.0	3.6		X-C7/9	0.002	-0.3	-180.4
	X-H5/6	0.002	-0.3	7.2		X-N10/11	0.002	-0.2	230.6
3cl(π)	X-C	0.029	-10.7	-446.0		X-H13/14	0.007	-1.9	-8.5
	X-N	0.054	-19.0	446.3		X-H15	0.002	-0.3	-5.3
	X-H	0.003	-0.7	-9.9	9br(σ)	X-C1	0.168	-72.8	-35.0
3br(π)	X-C	0.028	-10.0	-418.7		X-C2/6	0.060	-18.3	-30.3
	X-N	0.053	-17.8	422.5		X-C3/5	0.021	-4.0	-17.7
	X-H	0.003	-0.8	-10.3		X-C4	0.023	-3.9	-14.5
4f(π)	X-C	0.078	-39.0	-550.7		X-H13	0.053	-20.7	-41.8
	X-N	0.062	-24.6	253.4		X-H14/15	0.001	-0.1	-13.8
	X-H	0.006	-1.8	-17.2		X-C8/9	0.022	-6.4	-276.3
4cl(π)	X-C	0.066	-27.2	-422.9		X-C7	0.004	-0.6	-183.5
	X-N	0.054	-18.6	210.2		X-N11/12	0.015	-3.1	333.8
	X-H	0.007	-2.0	-18.6		X-N10	0.007	-0.7	228.9
4br(π)	X-C	0.065	-25.5	-393.1	10f(π)	X-C1/2/4/5	0.053	-23.8	-62.1
	X-N	0.054	-17.5	198.7		X-C3/6	0.053	-24.4	-64.4
	X-H	0.008	-2.1	-18.4		X-H/15/16	0.002	-0.4	-27.8
4f(σ)	X-C2	0.648	-510.7	-889.0		X-C7/8/9/10	0.006	-1.4	-314.0
	X-N5/7	0.134	-59.1	211.4		X-N11/12/13/14	0.003	-0.4	366.4
	X-N6/8	0.035	-11.6	189.2	10cl(π)	X-C1/2/4/5	0.050	-19.0	-42.6
	X-C1	0.034	-11.4	-317.9		X-C3/6	0.051	-20.0	-41.1
	X-H4	0.071	-30.2	-3.0		X-H/15/16	0.002	-0.6	-26.5
	X-H3	0.002	-0.3	2.3		X-C7/8/9/10	0.007	-1.9	-283.0
4cl(σ)	X-C1	0.129	-60.3	-438.7		X-N11/12/13/14	0.003	-0.6	329.0
	X-N6/8	0.077	-25.8	214.8	10br(π)	X-C1/2/4/5	0.050	-18.0	-38.8
	X-N5/7	0.035	-9.7	186.0		X-C3/6	0.051	-19.2	-36.6
	X-C2	0.037	-10.5	-357.6		X-H/15/16	0.003	-0.7	-25.8
	X-H3	0.032	-11.2	-29.6		X-C7/8/9/10	0.008	-2.1	-273.6
	X-H4	0.002	-11.1	10.7		X-N11/12/13/14	0.004	-0.7	318.2
4br(σ)	X-C1	0.104	-45.0	-406.0	10f(σ)	X-C3	0.720	-559.3	-595.3
	X-N6/8	0.069	-22.6	203.5		X-C2/4	0.109	-46.4	-24.2
	X-N5/7	0.039	-10.9	183.1		X-C1/5	0.018	-4.7	-22.4
	X-C2	0.041	-12.4	-353.1		X-C6	0.018	-3.7	-9.2
	X-H3	0.024	-7.8	-25.5		X-H15	0.070	-29.8	-23.9
	X-H4	0.003	-0.5	-12.6		X-H16	0.001	-0.2	-9.0

5f(π)	**X-C**	**0.037**	**-18.2**	**-866.4**		**X-C7/10**	**0.015**	**-4.4**	**-255.4**
	X-N	**0.075**	**-32.5**	**547.4**		**X-C8/9**	**0.002**	**-0.3**	**-189.3**
	X-F	**0.008**	**-2.3**	**266.6**		**X-N13/11**	**0.008**	**-1.6**	**318.7**
5f(σ)	**X-C3**	**0.607**	**-507.8**	**-1481.3**		**X-N12/14**	**0.002**	**-0.2**	**230.6**
	X-N4/5	**0.146**	**-69.6**	**487.0**	**10cl(σ)**	**X-C3**	**0.201**	**-95.4**	**-53.2**
	X-C1/2	**0.012**	**-2.8**	**-539.1**		**X-C2/4**	**0.076**	**-24.4**	**-39.0**
	X-N6	**0.012**	**-2.2**	**307.7**		**X-C1/5**	**0.025**	**-5.3**	**-25.1**
	X-F7	**0.170**	**-89.6**	**327.0**		**X-C6**	**0.031**	**-5.5**	**-19.0**
	X-F8/9	**0.003**	**-0.6**	**162.8**		**X-H15**	**0.048**	**-19.1**	**-46.3**
5cl(π)	**X-C**	**0.031**	**-12.7**	**-700.8**		**X-H16**	**0.002**	**-0.3**	**-14.7**
	X-N	**0.068**	**-25.4**	**450.8**		**X-C7/10**	**0.022**	**-6.6**	**-282.7**
	X-F	**0.011**	**-2.9**	**227.9**		**X-C8/9**	**0.003**	**-0.4**	**-210.0**
5br(π)	**X-C**	**0.030**	**-11.6**	**-659.6**		**X-N13/11**	**0.016**	**-3.1**	**330.0**
	X-N	**0.067**	**-23.8**	**425.6**		**X-N12/14**	**0.003**	**-0.4**	**249.7**
	X-F	**0.012**	**-3.1**	**217.2**	**10br(σ)**	**X-C3**	**0.168**	**-74.8**	**-41.4**
6f(π)	**X-C1/3/5**	**0.041**	**-16.4**	**-35.6**		**X-C2/4**	**0.072**	**-22.7**	**-36.3**
	X-C2/4/6	**0.038**	**-16.2**	**-223.3**		**X-C1/5**	**0.027**	**-5.7**	**-24.9**
	X-H	**0.002**	**-0.4**	**-18.0**		**X-C6**	**0.030**	**-5.5**	**-19.1**
	X-F	**0.005**	**-1.2**	**251.2**		**X-H15**	**0.044**	**-16.3**	**-41.5**
6cl(π)	**X-C1/3/5**	**0.038**	**-13.5**	**-21.3**		**X-H16**	**0.002**	**-0.2**	**-15.2**
	X-C2/4/6	**0.035**	**-12.6**	**-188.7**		**X-C7/10**	**0.023**	**-6.6**	**-275.1**
	X-H	**0.002**	**-0.5**	**-18.1**		**X-C8/9**	**0.003**	**-0.5**	**-209.3**
	X-F	**0.006**	**-1.5**	**218.3**		**X-N13/11**	**0.016**	**-3.2**	**320.8**
6br(π)	**X-C1/3/5**	**0.039**	**-13.2**	**-18.7**		**X-N12/14**	**0.004**	**-0.4**	**248.3**
	X-C2/4/6	**0.035**	**-12.1**	**-180.4**	**11f(π)**	**X-C1-6**	**0.058**	**-27.2**	**-82.0**
	X-H	**0.002**	**-0.5**	**-17.9**		**X-C7-12**	**0.006**	**-1.5**	**-322.8**
	X-F	**0.007**	**-1.7**	**209.7**		**X-N13-18**	**0.002**	**-0.4**	**355.1**
6f(σ)	**X-C6**	**0.659**	**-523.7**	**-863.8**	**11cl(π)**	**X-C1-6**	**0.054**	**-21.7**	**-57.0**
	X-C1/5	**0.102**	**-42.6**	**-5.2**		**X-C7-12**	**0.008**	**-2.1**	**-290.9**
	X-C2/4	**0.016**	**-3.5**	**-114.6**		**X-N13-18**	**0.003**	**-0.6**	**319.5**
	X-C3	**0.016**	**-2.6**	**1.5**	**11br(π)**	**X-C1-6**	**0.054**	**-20.6**	**-51.8**
	X-F11	**0.177**	**-92.8**	**316.2**		**X-C7-12**	**0.009**	**-2.4**	**-280.5**
	X-H7/9	**0.010**	**-3.6**	**-3.3**		**X-N13-18**	**0.004**	**-0.7**	**308.5**
	X-F10/12	**0.003**	**-0.5**	**155.5**	**11f(σ)**	**X-C6**	**0.724**	**-574.0**	**-640.3**
	X-H8	**0.001**	**-0.2**	**-2.6**		**X-C1/5**	**0.103**	**-44.1**	**-36.8**
7f(π)	**X-C1/3/4/6**	**0.042**	**-18.0**	**-241.8**		**X-C2/4**	**0.017**	**-4.1**	**-31.2**
	X-C2/5	**0.043**	**-17.4**	**-42.2**		**X-C3**	**0.015**	**-3.0**	**-20.7**
	X-F	**0.005**	**-1.2**	**249.7**		**X-C9**	**0.104**	**-51.1**	**-343.8**
	X-H	**0.002**	**-0.4**	**-21.4**		**X-C10/11**	**0.015**	**-5.2**	**-261.1**
7cl(π)	**X-C1/3/4/6**	**0.038**	**-14.0**	**-202.1**		**X-C7/12**	**0.002**	**-0.3**	**-184.9**
	X-C2/5	**0.040**	**-14.4**	**-26.5**		**X-C8**	**0.002**	**-0.3**	**-162.7**
	X-F	**0.007**	**-1.6**	**216.1**		**X-N18**	**0.033**	**-8.0**	**367.1**
	X-H	**0.002**	**-0.5**	**-21.3**		**X-N17/14**	**0.008**	**-1.7**	**305.4**
7br(π)	**X-C1/3/4/6**	**0.038**	**-13.4**	**-192.7**		**X-N13/16**	**0.002**	**-0.3**	**211.7**
	X-C2/5	**0.041**	**-14.0**	**-23.5**		**X-N15**	**0.004**	**-0.5**	**195.0**
	X-F	**0.008**	**-1.8**	**207.4**	**11cl(σ)**	**X-C5**	**0.731**	**-449.8**	**-33.1**
	X-H	**0.003**	**-0.6**	**-21.0**		**X-C4/6**	**0.112**	**-53.7**	**16.5**
7f(σ)	**X-C1**	**0.131**	**-74.3**	**-393.4**		**X-C1/3**	**0.032**	**-7.4**	**-14.6**
	X-C6	**0.066**	**-28.7**	**-280.6**		**X-C2**	**0.046**	**-8.6**	**-9.8**
	X-C2	**0.059**	**-20.3**	**-34.7**		**X-C10**	**0.103**	**-44.6**	**-164.3**
	X-C5	**0.022**	**-5.5**	**-20.6**		**X-C7/9**	**0.023**	**-6.9**	**-134.6**
	X-C3	**0.014**	**-3.5**	**-167.7**		**X-C8/11**	**0.003**	**-0.4**	**-103.0**
	X-C4	**0.014**	**-3.1**	**-154.6**		**X-C12**	**0.006**	**-0.8**	**-93.6**
	X-H11	**0.005**	**-1.2**	**-21.3**		**X-N14**	**0.059**	**-13.3**	**182.9**
	X-H12	**0.001**	**-0.2**	**-14.5**		**X-N13/18**	**0.018**	**-3.4**	**159.8**
	X-F9	**0.078**	**-33.8**	**328.4**		**X-N15/17**	**0.004**	**-0.5**	**118.8**
	X-F7	**0.023**	**-8.0**	**278.2**		**X-N16**	**0.013**	**-1.4**	**112.0**
	X-F8	**0.002**	**-0.3**	**180.4**	**11br(σ)**	**X-C4**	**0.385**	**-192.3**	**-39.4**
	X-F10	**0.002**	**-0.3**	**194.1**		**X-C3/5**	**0.107**	**-31.5**	**-32.2**
8f(π)	**X-C**	**0.046**	**-20.3**	**-271.2**		**X-C2/6**	**0.040**	**-8.6**	**-22.9**
	X-F	**0.005**	**-1.4**	**249.0**		**X-C1**	**0.063**	**-11.5**	**-18.2**
8cl(π)	**X-C**	**0.044**	**-16.6**	**-225.1**		**X-C7**	**0.094**	**-39.3**	**-238.3**
	X-F	**0.008**	**-2.0**	**215.4**		**X-C8/10**	**0.025**	**-7.0**	**-196.3**
8br(π)	**X-C**	**0.043**	**-15.6**	**-212.9**		**X-C9/12**	**0.003**	**-0.5**	**-153.0**
	X-F	**0.009**	**-2.2**	**205.2**		**X-C11**	**0.008**	**-1.1**	**-140.6**
8f(σ)	**X-C3**	**0.664**	**-532.1**	**-858.5**		**X-N13**	**0.071**	**-15.2**	**259.4**

	X-C2/4	**0.091**	**-37.4**	**-207.0**		**X-N14/15**	**0.022**	**-4.0**	**223.9**
	X-C1/5	**0.002**	**-2.6**	**-139.1**		**X-N16/18**	**0.005**	**-0.6**	**174.3**
	X-C6	**0.015**	**-2.7**	**-110.8**		**X-N17**	**0.018**	**-1.9**	**163.2**
	X-F10	**0.179**	**-93.4**	**297.1**					
	X-F8/11	**0.026**	**-10.4**	**234.1**					
	X-F9/12	**0.002**	**-0.4**	**145.0**					
	X-F7	**0.003**	**-0.4**	**124.6**					