Unlocking the Electronic Genome of Halogenobenzenes

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Supplementary Information:

 Table a.
 References for gas/solution phase halogenobenzene derivatives in Figure 2.

F	Full Sets ^{15, 16, 18}
Cl	Full Sets ^{17, 19}
Br	(1, 2c) ³⁹ , (2a, 2b, 3a) ¹⁸ , 3c ⁴⁰ , 4c ^{37, 40}
I	1 ¹⁸ , (2a,2b, 2c) ³⁸ , 3c ⁴⁰

Table b. Calculated HOMO-LUMO values and polarizabilities of seven altered benzene structures, gas phase. * - optimized benzene

Benzene structure number:	C-C distance (Å):	Е _в номо-шмо (eV):	Polarizabilities (A ³)
1	1.200	7.089	8.189
2	1.370	5.342	9.598
3*	1.397	5.112	9.868
4	1.418	4.940	10.063
5	1.430	4.836	10.185
6	1.470	4.525	10.593
7	1.600	3.642	12.061

Table c. Average C-C bond length vs. calculated HOMO-LUMO gaps for all hexahalogenated benzenes and optimized benzene; the increase in C-C bond length (past benzene) is induced by the steric effects of the halogens with the exception of fluorinated benzene where the average bond length is slightly smaller as compared to benzene

Structure:	C-C average bond length (Å):	HOMO-LUMO gap (eV):
C ₆ H ₆	1.397	5.112
C_6F_6	1.397	4.533
C ₆ Cl ₆	1.406	3.970
C ₆ Br ₆	1.407	3.144
C ₆ I ₆	1.413	1.545

Table d. Aromaticity (HOMA) indices of a, b and c types of four families (F, Cl, Br, & I) of halogenated benzene; structures of the a type have the lowest HOMA and c type structures highest aromaticity index across the entire group of halogens; structures 3c have the highest HOMA and HOMO-LUMO gap

Structure:	HOMA F	HOMA Cl	HOMA Br	HOMA I
2a	0.985	0.973	0.976	0.968
2b	0.991	0.984	0.984	0.980
2c	0.992	0.984	0.985	0.981
3a	0.986	0.958	0.961	0.942
3b	0.990	0.974	0.977	0.967
3c	0.996	0.984	0.986	0.979
4a	0.983	0.944	0.944	0.911
4b	0.990	0.959	0.961	0.942
4c	0.991	0.966	0.971	0.960

Table e. Comparison of polarizabilities and percent variation form experiment and as calculated with consistent and mixed basis sets with different exchange-correlation functionals. Green represents the best correlation with experiment. Blue is the second best fit to experiment. Red is the worst correlation with experiment.

Molecule	Polarizability (Å ³) and Percent Variation w/ EXP (parenthesis)					
	ЕХР	PBE with Def2-TZVP	PBE with aug-cc-pVTZ for halogens and Def2- TZVP for C and H	PBE with aug-cc-pVTZ for all atoms	B3LYP with Def2-TZVP	B3LYP with aug-cc-pVTZ
F ₂	1.38	0.89	1.26	1.26	0.89	1.22
Cl ₂	4.67	3.37	<mark>4.66</mark>	4.66	3.37	<mark>4.62</mark>
Br_2	7.02	5.55	<mark>6.83</mark>	6.83	5.51	<mark>6.77</mark>
I_2	10.8*	5.72	<mark>10.8</mark>		5.82	10.7
Benzene	10.32	9.87 (4.4%)	9.87 (4.4%)	10.60(2.1%)	9.65 (6.5%)	10.33 (0.5%)
Fluorobenzene	10.3	9.95 (3.4%)	10.09 (2.0%)	10.66 (3.5%)	9.69 (5.9%)	10.33 (0.3%)
<i>m</i> - Difluorobenzene	10.3	10.06 (2.3%)	10.32 (0.2%)	10.75 (4.4%)	9.75 (5.3%)	10.37 (0.7%)
Chlorobenzene	14.1/12.3	11.93 (3.0%)	12.40 (0.8%)	12.94 (5.2%)	11.63 (5.4%)	12.58 (2.3%)
<i>o</i> - Dichlorobenzene	14.17	13.88 (2.0%)	14.72 (3.9%)	15.16 (7.0%)	13.51 (4.7%)	14.71 (3.8%)
<i>m</i> - Dichlorobenzene	14.23	14.09 (1.0%)	14.99 (5.3%)	15.39 (8.2%)	13.70 (3.7%)	14.92 (4.8%)
<i>p</i> - Dichlorobenzene	14.20	14.16 (1.0%)	15.08 (6.2%)	15.44 (8.7%)	13.76 (3.1%)	14.97 (5.45%)
Bromobenzene	14.7	13.16 (10.5%)	13.73 (6.6%)	14.19 (3.5%)	12.82 (12.8%)	13.85 (5.8%)
Iodobenzene	15.5	13.86 (10.6%)	15.91 (2.7%)	16.43 (6.0%)	13.50 (14.8%)	15.96 (3.0%)

*Experimental polarizability of I_2 was estimated from the comparison of the atomic (**table 2** in **MS**) and diatomic polarizabilities of the other halogens. A value of 2.3 was used to multiply the polarizability of atomic iodine (4.7 Å³) to get the diatomic value (2.3 multiple is the average multiple from halogen atomic polarizabilities to diatomic polarizabilities for F through Br).

Table f. Comparison of energy gaps and percent variation form experiment (E_g^{opt}) and as calculated (E_g^{H-L}) with consistent and mixed basis sets with different exchange-correlation functionals. Green represents the best correlation with experiment. Blue is the second best fit to experiment. Red is the worst correlation with experiment.

Molecule	j	E_g^{H-L} (eV) and Percent Variation w/ EXP (parenthesis)				
	$\begin{array}{c} \text{EXP} \\ (E_g^{opt}) \end{array}$	PBE with Def2-TZVP	PBE with aug-cc-pVTZ for halogens and Def2- TZVP for C and H	PBE with aug-cc-pVTZ for all atoms	B3LYP with Def2-TZVP	B3LYP with aug-cc-pVTZ
F ₂	4.37	3.64 (16.7%)	<mark>3.63</mark>	3.63	7.24 (65%)	7.19
Cl_2	3.77	2.96 (21.5%)	<mark>2.90</mark>	<mark>2.90</mark>	4.91 (30.2%)	4.83
Br ₂	2.54	<mark>2.25</mark>	2.25 (11.4%)	<mark>2.25</mark>	3.92 (54.3%)	3.91
I ₂	2.17	<mark>1.71</mark>	1.71 (21.2%)	<mark>1.71</mark>	3.13 (44.2%)	<mark>3.15</mark>
Benzene	4.73	5.11 (8.1%)	5.11 (8.1%)	5.09 (7.6%)	6.65 (40.5%)	6.60 (39.5%)
Fluorobenzene	4.68	4.70 (0.3%)	4.71 (0.5%)	4.67 (0.1%)	6.27 (34.1%)	6.23 (33.2%)
<i>m</i> - Difluorobenzene	4.79	4.66 (2.7%)	4.67 (2.6%)	4.64 (3.1%)	6.26 (30.8%)	6.22 (29.9%)
Chlorobenzene	4.59	4.58 (0.1%)	4.60 (0.1%)	4.57 (0.5%)	6.15 (34.1%)	6.12 (33.3%)
<i>o</i> - Dichlorobenzene	4.50	4.41 (2.1%)	4.42 (1.9%)	4.39 (2.4%)	5.98 (32.8%)	5.94 (32.1%)
<i>m</i> - Dichlorobenzene	4.49	4.43 (1.4%)	4.43 (1.3%)	4.41 (1.8%)	5.99 (33.4%)	5.96 (32.6%)
<i>p</i> - Dichlorobenzene	4.43	4.19 (5.4%)	4.21 (5.0%)	4.18 (5.7%)	5.76 (30.1%)	5.74 (29.5%)
Bromobenzene	4.59	4.50 (2.0%)	4.50 (2.0%)	4.47 (2.6%)	6.06 (32.1%)	5.98 (30.3%)
Iodobenzene	4.57	4.22 (7.7%)	4.06 (11.2%)	4.05 (11.4%)	5.69 (24.5%)	5.46 (19.6%)

 Table g.
 List of linear relationships as established in Figures 4, 9, and 11.

Figure 4:

Figure 4a			Figure 4b	
Cl	y = -0.0577x + 5.2651	R ² = 0.7439	y = -0.0576x + 5.2742	$R^2 = 0.9563$
Br	y = -0.08x + 5.6557	$R^2 = 0.9342$	y = -0.0801x + 5.6382	$R^2 = 0.9869$
I	y = -0.0864x + 5.5266	$R^2 = 0.907$	y = -0.0896x + 5.5852	$R^2 = 0.9856$

Figures 9 and 11:

Figure 9			Figure	2 11
Cl	y = -51.722 x + 76.552	$R^2 = 0.4844$	y = 7.5181x - 3.0307	$R^2 = 0.4944$
Br	y = -131.75x + 188.03	$R^2 = 0.7728$	y = 20.18x - 15.684	R ² = 0.8145
Ι	y = -167.08x + 236.92	$R^2 = 0.9081$	y = 19.829x - 15.894	$R^2 = R^2 = 0.9093$











Additional Interesting Observations Regarding the MOs and Fig 7:

1) The calculated LUMO energies for F-BZs in **Fig 7** are always lower than that predicted for benzene (see **Fig X**). In contrast, while the HOMO energies of F-BZs start *higher* than that of benzene, by the tri-substituted structures the HOMO energies are below the HOMO energies of BZ.

2) A direct correlation between %X_{LUMO} and the energy of the LUMO exists.

3) Upon comparison of the $\% X_{LUMO}$ for each structure in a substitution group, multiples exists which allows the smallest $\% X_{LUMO}$ value in the group to be equal to others in the group (see **Fig e** in **SI**). These $\% X_{LUMO}$ multiples, which relate the $\% X_{LUMO}$ values of the *a*-, *b*- and *c*-structures, lessen as the IP of the halogens decrease (approaching a value of 1). A clear example is seen in the tri-substituted groups; for F-BZs, a multiple of 2.0 is need to equate $\% X_{LUMO}$ value of 3b to 3a and a multiple of 2.3 is needed to equate the 3b and 3c values. The same multiples for Cl-BZs are only 1.7 and 1.9 for 3a *vs* 3b and 3b *vs* 3c, respectively. For Br-BZs and I-BZs the $\% X_{LUMO}$ multiple is 1.0 for all comparisons. As the $\% X_{LUMO}$ multiple between structures lessens, the $E_g^{H-L} vs$ structure plot flattens out and/or softens (see **Fig 3**). Once the $\% X_{LUMO}$ multiple between all structures in a group is 1.0, the *a*-structure will always have the smallest E_g^{H-L} and the *c*-structure will have the largest (this is a steric/aromaticity effect discussed in **Sec**

3.5). It is also interesting to note that as the IP/electronegativity of the halogen decreases for a given structure (e.g., 2a or 3b, etc.) the $%X_{LUMO}$ and $%X_{HOMO}$ always increases and E_q^{H-L} always decreases.

4) The F-BZs and Cl-BZs, as well as the mono- and di-substituted Br-BZs, have large differences in the $\% X_{LUMO}$ values. This is a result of the differing symmetries and/or the varying positions of the halogen nuclei *wrt* the nodes of the benzene MOs. Comparison of the halogen AO interactions with the benzene MOs in the 2a *vs* 2b structures shows nearly identical interaction of the electron densities associated with that of the halogen AOs and benzene MOs (see **Fig g** in **SI**). This results in nearly identical $\% X_{LUMO}$ values in the case of F-BZs, and small variations for Cl-BZs and Br-BZs. In contrast, the halogens in 2c structures sit in a node of the benzene MOs. This contributes to the relatively low $\% X_{LUMO}$ values of the 2c structures when compared to the 2a and 2b structures. Similar trends can be seen for the higher substituted F-BZ and Cl-BZ structures.

Inspection of the LUMOs associated with the tri- or higher substituted Br-BZs, and all I-BZs, shows that the electron density distribution between the halogen AOs and the benzene MOs is nearly uniform from a- to b- to c-structures (it's just moved around the ring). This is why the %X_{LUMO} multiple when comparing structures is 1.0 for these groups.

<pre># Benzene input template ! RKS PBE SlowConv Tigh*</pre>	e tSCF def2-TZVP def2	2-TZVP/J Normalprint OPT PA	L8	
%scf MaxIter 1000 TolE 1E-7 TolErr 1E-6				
ena				
Bolan 1				
end				
* xvz 0 1				
C 1.7151000000	-1.3341000000	0.0007000000		
C 3.2551000000	-1.3341000000	0.0008000000		
C 4.0252000000	-0.0004000000	0.0007000000		
C 3.2551000000	1.3332000000	0.000300000		
C 1.7151000000	1.3332000000	-0.0001000000		
C 0.9452000000	-0.0005000000	0.000000000		
H 1.145100000	-2.3214000000	0.001000000		
H 3.8251000000	-2.3214000000	0.0011000000		
H 3.825000000	2.3205000000	0.000400000		
H 1.1451000000	2.3204000000	-0.000600000		
H 5.1651000000	-0.0003000000	0.000800000		
H -0.1948000000	-0.0005000000	-0.0004000000		
*				
%plots format cube				
dim1 100 dim2 100 dim3 100				
<pre>SpinDens("Benzene.cube"); end</pre>				

Benzene.inp A template input file for ORCA detailing the calculation type and level of theory utilized in this study.







Figure I Molecular orbital diagram of Benzene (left; green lettering), 1 Fluorobenzene (center; purple lettering) and Fluorine atom (right; red lettering). Occupied orbitals are represented by blue lines and unoccupied orbitals have orange lines.

Figure m Molecular orbital diagram of Benzene (left; green lettering), 1 Chlorobenzene (center; purple lettering) and Chlorine atom (right; red lettering). Occupied orbitals are represented by blue lines and unoccupied orbitals have orange lines

Figure n Molecular orbital diagram of Benzene (left; green lettering), 1 Bromobenzene (center; purple lettering) and Bromine atom (right; red lettering). Occupied orbitals are represented by blue lines and unoccupied orbitals have orange lines.

Figure o Molecular orbital diagram of Benzene (left; green lettering), 1-lodobenzene (center; purple lettering) and lodine atom (right; red lettering). Occupied orbitals are represented by blue lines and unoccupied orbitals have orange lines