Electronic Supplementary Information

Probing the O…Br-Br halogen bonding in the x-ray crystal structures with *ab initio* calculations

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Cartesian coordinates for 1-6 at MP2/6-311+G* level of theory.

1

C	3.65471100	0.73330900	0.02185200
O	2.94497600	-0.50397700	-0.05783800
H	4.71520600	0.59534500	-0.20551400
H	3.21354700	1.38654800	-0.72781300
H	3.54571200	1.19637500	1.00670500
H	3.30882900	-1.12521000	0.58044700
Br	0.28864700	-0.20945800	-0.02418900
Br	-2.01068600	0.14028300	0.01498200

2

O	2.64395300	-0.00009000	-0.34031800
C	3.21356800	-1.17077200	0.22417000
H	3.03110800	-1.21322100	1.30499800
H	2.73728000	-2.02304000	-0.25831300
H	4.29345900	-1.20149200	0.03771700
C	3.20451400	1.17612400	0.22178900
H	3.02303900	1.21863100	1.30279600
H	4.28386000	1.21557400	0.03394500
H	2.72023900	2.02362100	-0.26114100
Br	0.01868400	-0.00219700	-0.16071200
Br	-2.29723000	0.00072700	0.10033400

3eq

O	-4.34336400	0.00080100	0.52443900
C	-3.76985000	1.16196000	-0.06282300
C	-2.26491700	1.17023900	0.12636900
O	-1.68914200	-0.00057200	-0.46078700
C	-2.26596800	-1.17067300	0.12675800
C	-3.77089800	-1.16106000	-0.06245100
H	-4.00915600	1.19470800	-1.13604600
H	-4.22829700	2.02221500	0.43104000
H	-2.01763700	1.19949500	1.19699400
H	-1.80392000	2.02547200	-0.37336100
H	-2.01871600	-1.19980400	1.19739200
H	-1.80576900	-2.02648900	-0.37270900
H	-4.01021200	-1.19392500	-1.13566800
H	-4.23014400	-2.02074200	0.43167000
Br	0.91546400	-0.00042900	-0.19213900
Br	3.22207000	0.00027000	0.14883500

3_{ax}

O	-3.61015100	0.02558900	1.12344000
C	-2.86515600	-1.14423700	0.80526500
C	-2.54399200	-1.18554000	-0.67700500
O	-1.80743400	-0.02261200	-1.06423100
C	-2.54015600	1.15766500	-0.72541900
C	-2.86168600	1.17900800	0.75720100
H	-1.93486300	-1.16572300	1.39113100
H	-3.48476100	-1.99752100	1.09210800
H	-3.47194700	-1.23295000	-1.26371800
H	-1.91713800	-2.04530000	-0.92593900
H	-3.46812200	1.18350100	-1.31351000
H	-1.91128700	2.00485100	-1.00999500
H	-1.93179600	1.22254200	1.34253400
H	-3.47909900	2.04524100	1.00772400
Br	0.73651500	-0.00978800	-0.35367700
Br	2.97221700	0.00750700	0.30355600

4eq

C	2.31430000	-1.14559600	0.09624200
O	1.72316300	0.00864400	-0.47209400
C	2.28070700	1.18955400	0.11788700
C	3.79057900	1.19323700	-0.07515800
H	2.11933100	-1.14675500	1.18302100
H	1.85318300	-2.00516500	-0.38618000
H	2.02072800	1.21180100	1.18749200
H	1.79501900	2.03271800	-0.37537400
H	4.01726700	1.27237600	-1.14216300
H	4.23918300	2.05120100	0.43878800
Br	-0.92722600	-0.00789300	-0.19558400
Br	-3.22858100	0.00605000	0.15588400
C	4.35752000	-0.11356100	0.46411300
H	4.23266100	-0.16917700	1.55695500
H	5.41612400	-0.23335100	0.22998500
O	3.68947800	-1.22001500	-0.14309800

4ax

C	-2.58454500	-1.32150500	-0.02803800
O	-1.84876200	-0.53506000	-0.94414300
C	-2.52994000	0.69953700	-1.20059200
C	-2.77179100	1.44216800	0.10667200
H	-3.57346000	-1.54027300	-0.46710700
H	-2.01532500	-2.23565500	0.13004300
H	-3.48058100	0.47776700	-1.70877700
H	-1.89195500	1.25958900	-1.88593000
H	-1.81372500	1.75187100	0.53319300
H	-3.37414900	2.34049900	-0.07172600

Br	0.72523300	-0.19037900	-0.28897100	H	-1.98237100	1.74584500	-0.31459700
Br	2.96276400	0.15289200	0.25243400	H	-5.21277000	0.08514100	0.84313200
C	-3.47875900	0.50835400	1.08076500	H	-5.16456500	-0.22462700	-0.88870200
H	-4.49562600	0.27486200	0.72710000	H	-4.69917700	-1.52138800	0.24091000
H	-3.54986600	0.93361400	2.08271600	Br	0.39761100	-0.27422900	-0.02029400
O	-2.73811300	-0.70513600	1.21744900	Br	2.68257000	0.14915300	0.01793600
5				**6**			
C	-3.23192100	0.02331900	-0.00528100	C	2.63509300	2.71119700	0.00000000
O	-2.30353400	-0.77430300	-0.03622100	O	1.42614700	2.84850600	0.00000000
C	-3.00625000	1.51751800	-0.02130900	Br	0.00000000	0.42157600	0.00000000
C	-4.66575000	-0.44764400	0.06019200	Br	-0.96091500	-1.68872200	0.00000000
H	-3.71167900	2.01254100	-0.69369700	H	3.10258300	1.71247500	0.00000000
H	-3.18398000	1.91542300	0.98363400	H	3.30971000	3.58238400	0.00000000

Cartesian coordinates for 1-6 at CBS-QB3 level of theory.

1				H	-2.69971700	2.02760700	-0.27277900
C	3.64319100	0.69876000	0.02860800	Br	-0.05026600	-0.00028300	-0.13854700
O	2.89656300	-0.52235000	-0.03275200	Br	2.32012600	0.00010600	0.08618000
H	4.71456900	0.49434100	0.12329400	**3_{eq}**			
H	3.46634500	1.21904400	-0.91143900	O	4.36745500	0.00032200	0.45503600
H	3.31613700	1.33768400	0.85511800	C	3.77663900	-1.17058900	-0.09722500
H	3.01703800	-0.99971400	0.79500500	C	2.27536900	-1.18529500	0.15466300
Br	0.32845200	-0.18582900	-0.04953800	O	1.68066100	-0.00027300	-0.39821100
Br	-2.02975900	0.12682600	0.02749200	C	2.27489100	1.18505000	0.15458400
2				C	3.77615400	1.17095200	-0.09731100
O	-2.63142600	0.00002300	-0.33683900	H	3.97076400	-1.21812600	-1.17882900
C	-3.19760300	-1.18575100	0.20817300	H	4.25546400	-2.02476100	0.38543300
H	-4.27293800	-1.22657000	-0.00391900	H	2.07051700	-1.22911200	1.23196400
H	-2.70167300	-2.02751000	-0.27269700	H	1.79424200	-2.03104300	-0.33814400
H	-3.04110700	-1.24091500	1.29258400	H	2.07003000	1.22883500	1.23189000
C	-3.19668900	1.18639100	0.20793100	H	1.79333400	2.03052000	-0.33827400
H	-4.27189100	1.22819300	-0.00465200	H	3.97026500	1.21849900	-1.17891900
H	-3.04062800	1.24139000	1.29240500	H	4.25463000	2.02534400	0.38529300

Br	-0.89056100	-0.00009000	-0.15136500
Br	-3.25751000	0.00005400	0.11298600

3_{ax}

O	-3.74752400	0.00183600	1.01960300
C	-2.98557700	-1.17149000	0.75242000
C	-2.52337800	-1.18839300	-0.69718000
O	-1.77611900	-0.00152300	-1.00309000
C	-2.52250800	1.18666300	-0.70020600
C	-2.98454000	1.17382200	0.74947500
H	-2.11422800	-1.21790200	1.42157000
H	-3.63549000	-2.02367300	0.96046700
H	-3.38955100	-1.23971300	-1.36986900
H	-1.86116900	-2.03093700	-0.90130600
H	-3.38875400	1.23683000	-1.37288900
H	-1.85974100	2.02820600	-0.90664200
H	-2.11307000	1.22104200	1.41841200
H	-3.63363500	2.02711700	0.95550000
Br	0.73907800	-0.00065000	-0.31411800
Br	3.04037400	0.00044700	0.28656300

4eq

C	2.29299400	-1.15849500	0.10515100
O	1.70428100	0.02155600	-0.43582900
C	2.28969600	1.20580500	0.13316700
C	3.80165200	1.18963300	-0.08785900
H	2.10893700	-1.18260700	1.19261200
H	1.81370300	-1.99970100	-0.38971300
H	2.05183000	1.24460300	1.20568200
H	1.80709100	2.04909700	-0.35941900
H	4.01179800	1.28125000	-1.15667200
H	4.26633600	2.03615000	0.42769600
Br	-0.89474400	-0.00023300	-0.16928600
Br	-3.25351600	0.00228200	0.13327600
C	4.36764600	-0.13387000	0.42592700
H	4.28205700	-0.19034400	1.52211800
H	5.41491900	-0.26540900	0.15491900
O	3.66078200	-1.22945400	-0.16356600

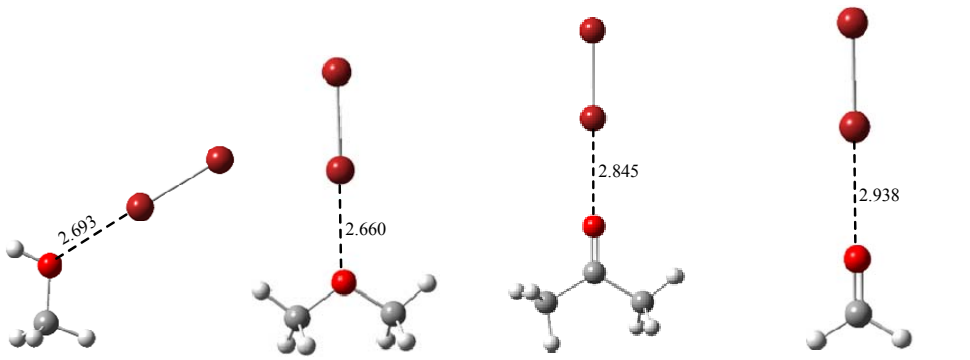
4_{ax}

C	-2.56677300	-1.29348000	-0.34676700
O	-1.80498200	-0.28584700	-0.99953100
C	-2.49124300	0.97886500	-0.99204300
C	-2.85909700	1.37798700	0.43598500
H	-3.50396400	-1.43330100	-0.91276200
H	-1.96601100	-2.19976500	-0.36168200
H	-3.39153900	0.88458900	-1.61582400
H	-1.81726900	1.69253400	-1.46436200
H	-1.94697300	1.59689700	0.99718700
H	-3.48004000	2.27946800	0.42798300
Br	0.71923800	-0.10574300	-0.30529400
Br	3.01536200	0.08300900	0.27726600
C	-3.60107300	0.21946300	1.10328300
H	-4.58851900	0.07516600	0.63750400
H	-3.74553700	0.38643700	2.17033400
O	-2.84027100	-0.98707200	0.98701200

5

C	-3.14364400	0.03276200	-0.00380500
O	-2.22918000	-0.77072500	-0.00087600
C	-4.57797700	-0.44725200	0.00734400
C	-2.91775000	1.52636400	-0.00627800
H	-4.61149200	-1.52179900	0.17844200
H	-5.15646700	0.07805300	0.77262300
H	-5.04179700	-0.21862800	-0.95808900
H	-3.63182000	2.03178900	-0.66086600
H	-3.08673200	1.90520600	1.00802800
H	-1.89685600	1.76310200	-0.30073200

Br	0.32874100	-0.27221900	-0.00200300	O	1.07874300	2.88238900	0.00000000
Br	2.67396900	0.14241400	0.00154700	Br	0.00000000	0.45221700	0.00000000
				Br	-0.80154700	-1.77961200	0.00000000
6				H	2.89972000	2.00241100	0.00000000
C	2.28352800	2.91901400	0.00000000	H	2.82331500	3.88320900	0.00000000



	1': Methanol:Br_2	**2': Dimethyl ether:Br_2**	**5': Acetone:Br_2**	**6': Formaldehyde:Br_2**
B.E =	**-4.0**	**-4.2**	**-2.5**	**-2.3**

Fig. S1 MP2/6-311+G* optimized geometries of σ-type interaction for methanol, dimethyl ether, acetone and formaldehyde with bromine molecule. [Distances are in Å] [BSSE corrected binding energies given in kcal/mol] [Gray = carbon; white = hydrogen; red = oxygen; dark red = bromine]

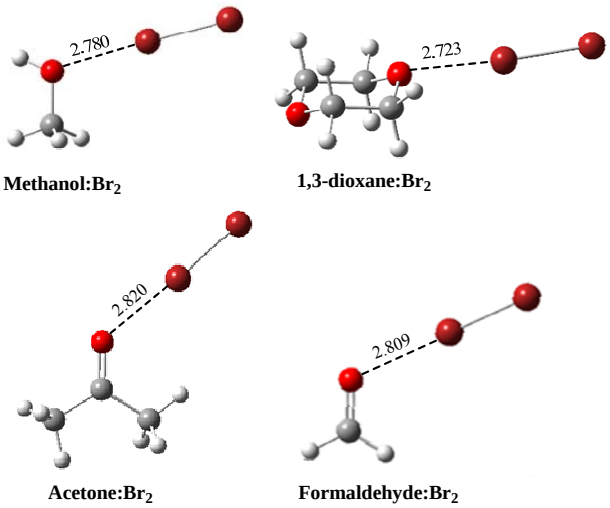


Fig. S2 Different geometries of methanol, 1,3-dioxane, acetone and formaldehyde with bromine molecule taken from x-ray crystal structure. [Distances are in Å] [Gray = carbon; white = hydrogen; red = oxygen; dark red = bromine]

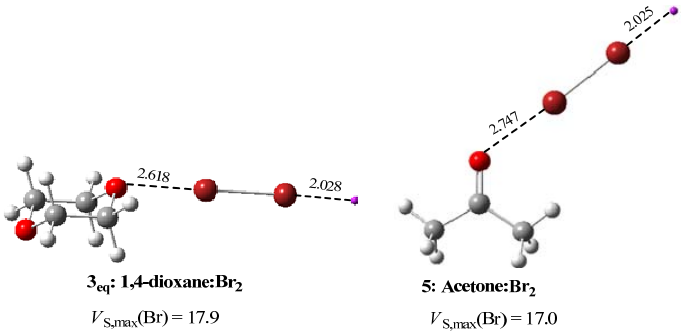


Fig. S3 The maximum electrostatic potentials ($V_{S,max,}$kcal/mol) of bromine atom for 1,4-dioxane:Br_2 and acetone:Br_2 complexes. The distances are given in A. [Gray = carbon; white = hydrogen; red = oxygen; dark red = bromine]

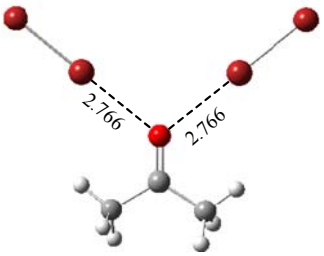


Fig. S4 MP2/6-311+G* optimized bridging geometry of acetone with bromine molecule. [Distances are in Å] [Binding energies (BSSE corrected) are in kcal/mol] [Gray = carbon; white = hydrogen; red = oxygen; dark red = bromine]

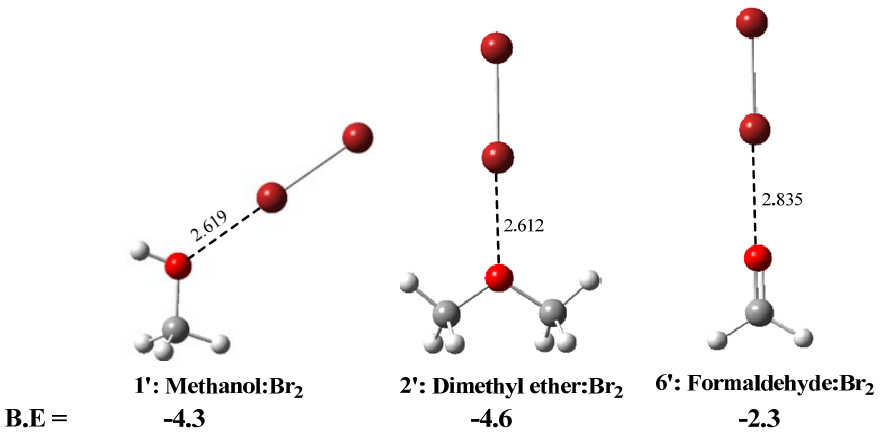


Fig. S5 CBS-QB3 optimized geometries of σ-type interaction for methanol, dimethyl ether and formaldehyde with bromine molecule. [Distances are in Å] [Binding energies are in kcal/mol] [Gray = carbon; white = hydrogen; red = oxygen; dark red = bromine]