

Table S1. Selected crystal data of 1,2-, 1,3- and 1,4-isomers of dibromo- and dichlorobenzenes.

	1,2dBrB ^b	1,3dBrB ^b	1,4dBrB ^c
mol. sym.	C_{2v} (<i>mm2</i>)	C_{2v} (<i>mm2</i>)	D_{2h} (<i>mmm</i>)
space group, Z'	<i>Pbca</i> , 1	<i>P2₁2₁2₁</i> , 2	<i>P2₁/a</i> , 0.5
m.p., K ^a	256.15	248.45	326.25
T _{meas} , K	250 K	260 K	293
d_x , g ml ⁻¹	2.242	2.234	2.342
Br···Br/molecule	2	2	4
d(Br···Br), Å	3.7622(14)	3.7642(16)	3.758
		3.7725(14)	
	12dClB ^d	13dClB ^d	14dClB ^e
mol. sym.	C_{2v} (<i>mm2</i>)	C_{2v} (<i>mm2</i>)	D_{2h} (<i>mmm</i>)
space group, Z'	<i>P2₁/n</i> , 1	<i>P2₁/a</i> , 2	<i>P2₁/a</i> , 0.5
m.p., K ^a	280.25	266.15	360.45
T _{meas} , K	223	220	293
d_x , g ml ⁻¹	1.535	1.517	1.523
Cl···Cl/molecule	2	1.5	4
d(Cl···Cl), Å	3.574	3.695	3.806(2)
		3.460	

^a Martin, Yalkowsky & Wells (1979)

^b This work

^c Bezzi & Croatto (1942) and Croatto & Bezzi (1949)

^d Boese *et al.* (2001)

^e Estop *et al.* (1997)

Table S2. Halogen···halogen distances and C-halo···halo angles in dihalobenzenes crystal structures.

	12dBrB ^a	13dBrB ^a	14dBrB ^b
d(Br···Br)	d(Br1···Br2 ⁱ) = d(Br2···Br1 ⁱⁱ) = 3.7622(14)	d(Br1B···Br1B ⁱⁱⁱ) = d(Br1B···Br1B ^{iv}) = 3.7642(16) d(Br3A···Br3B ^v) = d(Br3B···Br3A ^{vi}) = 3.7725(14)	d(Br1···Br1 ^{vii}) = d(Br1···Br1 ^{viii}) = 3.758
ang(C-Br···Br)	(C1-Br1···Br2 ⁱ) = 155.9(2) (C2-Br2···Br1 ⁱⁱ) = 133.3(2)	(C1B-Br1B···Br1 ⁱⁱⁱ) = 129.5(3) (C1B ⁱⁱⁱ - Br1B ⁱⁱⁱ ···Br1B) = 158.3(2) (C3A-Br3A···Br3B ^v) = 168.2(3) (Br3A···Br3B ^v -C3B ^v) = 79.7(2)	(C1-Br1···Br1 ^{viii}) = 94.3 (C1-Br1···Br1 ^{vii}) = 164.9

ⁱ = 0.5-x, 1-y, -0.5+z; ⁱⁱ = 0.5-x, 1-y, 0.5+z; ⁱⁱⁱ = 0.5+x, 0.5-y, 1-z; ^{iv} = -0.5+x, 0.5-y, 1-z; ^v = 1-x, 0.5+y, 1.5-z; ^{vi} = 1-x, -1.5+y, 1.5-z; ^{vii} = -0.5+x, 1.5-y, z; ^{viii} = -0.5+x, 0.5-y, z.

	12dClB ^c	13dClB ^c	14dClB ^d
d(Cl···Cl)	d(Cl1···Cl2 ⁱ) = d(Cl2···Cl1 ⁱ) = 3.574	d(Cl2···Cl3 ⁱⁱⁱ) = d(Cl3···Cl2 ^{iv}) = 3.695 d(Cl4···Cl4 ^v) = 3.460	d(Cl···Cl ^{vi}) = 3.806(2) d(Cl···Cl ^{vii}) = 3.806(2)
ang(C-Cl···Cl)	(C1-Cl1···Cl2 ⁱ) = 94.2 (C2-Cl2···Cl1 ⁱⁱ) = 170.1	d(C3- Cl2···Cl3 ⁱⁱⁱ) 163.3 d(C7-C3···Cl2 ^{iv}) 81.0 (C9-Cl4···Cl4 ^v) = 146.8 (C9 ^v -Cl4 ^v ···Cl4) = 146.8	(C1-Cl1···Cl1 ^{vi}) = 92.5 (C1-Cl1···Cl1 ^{vii}) = 166.7

ⁱ = -0.5-x, -0.5+y, 1.5-z; ⁱⁱ = -0.5-x, 0.5+y, 1.5-z; ⁱⁱⁱ = -1+x, -1+y, z; ^{iv} = 1+x, 1+y, z; ^v = 1-x, 2-y, -z; ^{vi} = 0.5-x; 0.5+y; 1-z; ^{vii} = 0.5-x, -0.5+y, 1-z.

^a This work

^b Bezzi & Croatto (1942) and Croatto & Bezzi (1949)

^c Boese *et al.* (2001)

^d Estop *et al.* (1997)