

Halogen bonds in some dihalogenated phenols. Applications to crystal engineering.

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S1. Computational Methodology

The experimental structure of 3,4-dichlorophenol at -123°C was taken as an input in the crystal structure prediction (CSP) of **1,2** and **3**. The structure was then optimized and ESP charges were assigned in DMol3 component of Materials Studio. Optimized structures were taken as input structures in CSP protocol. For **2** and **3**, the same procedure of optimization was followed after respective substitutions. The CSP protocol has been detailed below:

Protocol: Packing >> Clustering >> Geometry Optimization >> Clustering

Version: 6.0

---- Packing parameters ----

Search algorithm	:	MC Simulated Annealing
Maximum number of steps	:	7000
Explore torsions	:	No
Pre-optimize structures	:	No
Steps to accept before cooling:	:	20
Minimum move factor	:	0.1000E-06
Heating factor	:	0.02500
Maximum temperature	:	100000.0 K
Minimum temperature	:	300.0 K

---- Cluster analysis parameters ----

Cluster grouping	:	Forcefield type
Cutoff	:	7.000
Number of bins	:	140
Tolerance	:	0.2000
Maximum number of clusters	:	All clusters

---- Geometry optimization parameters ----

Algorithm	:	Smart
Convergence tolerance:	:	
Energy	:	0.001 kcal/mol
Force	:	0.5 kcal/mol/A
Maximum number of iterations	:	500
External pressure	:	0 GPa
Motion groups rigid	:	YES
Optimize cell	:	YES

---- Energy parameters ----

Forcefield : COMPASS26

Electrostatic terms:

Summation method : Ewald
Accuracy : 0.001 kcal/mol
Buffer width : 0.5 Å

van der Waals terms:

Summation method : Ewald
Accuracy : 0.001 kcal/mol
Repulsive cutoff : 6 Å
Buffer width : 0.5 Å

S2. Database Studies: Cl/Br isostructurality

A. Type I: 64 pairs (67.4%)

RIGLID	RUFGOP	ONEDAR	VEJGUN	JEBGAZ
RIGLOS	VIDFEU	ONEDIV	VEJHAV	AFEQIM
CLANTO	IFULUQ04	NAGVUM	IWOXIB	CLURAC10
BRANTO	WASHEE	OHIJAR01	XEHOL	BRURAC11
NUYJUM	MUTBEJ	MEHGAI	XICPEF	ZZVTY12
NUYKAT	MUTBOT	GEPNEV	QOKFIG	TPHMBR02
QEDXEC	HALDOL01	OLOHIG	SULTOJ	TAQBUJ
YIHZAQ	BIBSEK	ROFBIIY	SULTUP	TAQCAQ
KAJFUX	XUBPIT	DUPTOY	HOFKET	ULUPIA
KAJFIL	XUBPOZ	FEYVAH	KUSNIW	JAMXEB
SEHHIX02	TIKTOX	WOGYAT	QOKKAY	MOSWAT
SAZZAV	TIKTIR	DUDCUB	PIDROK	SOYTUW
OGEKUH	XOBKEE	HUMHUS	QALNOH	LEMLEV
WADGAL	XOBKII	YIZRAB	QALNUN	LEMLIZ
ADALUN	PUZZAM	MIGXAC	QERTIR	CBZCAN01
RODGIA	UDURAN	SEZFEJ	SEZNUH	MBZCLD10
TIZVUU	NISCOI01	SUZKUU	KOFFIV	QAKBOU
TIZWAB	NOLYET01	SUZZIX	BOQWEJ	QAKBUA
YAKWUC	JEPYAF	SIRXAT	ISOBUE	SUZGUQ
YAKXAJ	JEPZIO	VASMEI	ISOCAV	TUPSUT
CAVQIZ	TINWET	NULROC	SAZZID	GEPNUL
ULELON	MODWOS	NULRUI	SAZYOI	AFEHOJ
NULSAP	JEPXUY	SEHHET	VOQREZ	SACTAS
NULSET	JEPZEK	SAZYUO	HODPOG	CACSOP
NULQUH	COTMON	COBBEA	SEFYUX	
NULRAO	TEJSIK	CILYUF	VITVID	

Type II: 31 pairs (32.6%)

DOZJAD	GACFOF	MUVBAG	COXNEI	CBALOS01
ZUYZAU	HEJNEP	MUTZUW	BRGUOS01	BAGWOW
YICFAR	GAKNAH	CLDOUR	BAJVUD	HECKOP

YICFEV	IJUXEQ01	BROXUR11	YUNWOU	YUHZAC
XOXKAX	BNQDCP	MECINT	MOKMIJ	IGEHEI
XOXKEB	BNQDBP	MBRCIN	CUDDEL	IGEHIM
CPHACR	TIHZOA	DIRNOH	ODEPUJ	DUPFUQ
BPHACR	TIHZEQ	TOHTUG	BPCBZS11	PUJKIP
NABRAJ	RALNEY	OFIWAB	AJETOZ	YAYVIE
BRBZAM	HEWRIL	OFIWEF	DUJJOI	YAYVUQ
OMEGUJ	TIHYOZ	TIHWUD	AMCLPY	SETGII
OMEHAQ	TIHYEP	BPCBZS11	CAJXAN	HIRQIJ
NEBFAB				
NEBFEF				

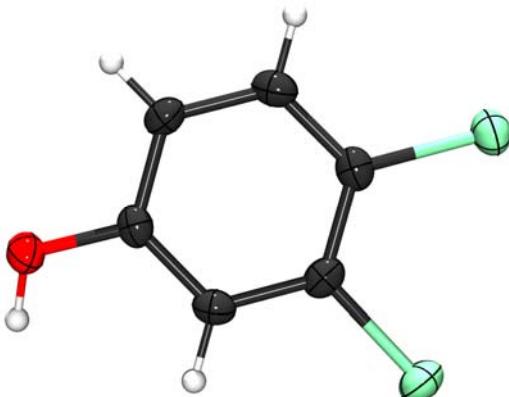
S3. Hydrogen bond table

All distances obtained at $-123\text{ }^{\circ}\text{C}$ are neutron normalized.

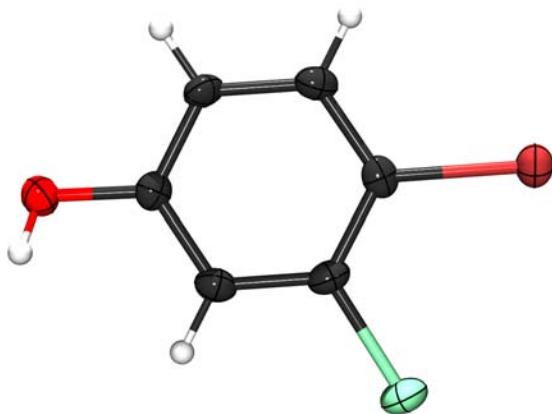
	D–H…A	Symmetry code	D–H (Å)	H…A (Å)	D–H…A (°)
3,4-Dichlorophenol (1)	O1–H1O…O1	7/4–y,1/4+x,1/4+z	0.98	1.74	171
4-Bromo-3-chlorophenol (2)	O1–H1O…O1	1/4+y,5/4–x,1/4+z	0.98	1.76	169
3-Bromo-4-chlorophenol (3)	O1–H1O…O1	1–x,1/2+y,–1/2–z	0.98	1.69	170
4-Chloro-3-iodophenol (4)	O1–H1O…O1	1–x,–1/2+y,3/2–z	0.98	1.73	165
3,5-Dibromophenol (5)	O1–H1O…O1	–1–x,1/2+y,3/2–z	0.98	1.71	176

S4. ORTEP diagrams

3,4-Dichlorophenol (1)



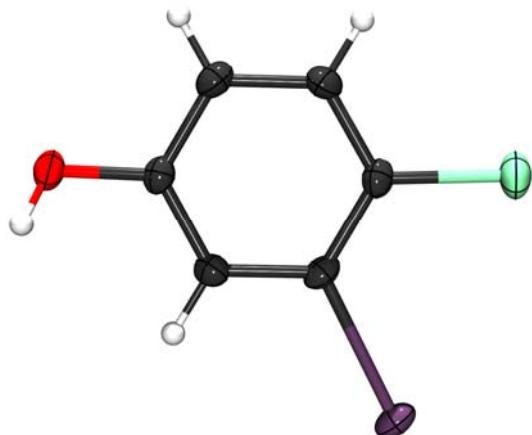
4-Bromo-3-chlorophenol (2)



3-Bromo-4-chlorophenol (3)



4-Chloro-3-iodophenol (4)



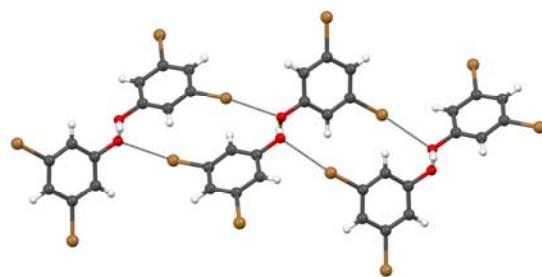
3,5-Dibromophenol (5)



S5. Video showing elastic deformation in 2

Videos are provided as separate files.

S6. Crystal structure of 3,5-dibromophenol (5)



S7. Crystallographic table for 4-chlorobenzoic acid and 2,3,5-trichlorosalicylic acid

Name	4-Chlorobenzoic acid	2,3,5-Trichlorosalicylic acid
Formula	C ₇ H ₅ ClO ₂	C ₇ H ₃ Cl ₃ O ₃
Molecular weight	156.56	241.44
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 ₁ /c
a (Å)	3.8017(8)	4.9531(14)
b (Å)	6.1607(12)	24.020(6)
c (Å)	14.208(3)	8.007(3)
α (°)	92.417(7)	90
β (°)	94.718(7)	118.88
γ (°)	92.286(7)	90
Volume (Å ³)	331.03(12)	834.2(5)
Z	2	4
ρ _{calc} (g/cm ³)	1.571	1.923
F(000)	160	480
μ (MoK _α) (mm ⁻¹)	0.499	1.062
Temp. (K)	150K	150K
θ Range for data collection (°)	3.3, 27.5	1.7, 27.6
R ₁	0.0347	0.0468
wR ₂	0.0977	0.1452
Goodness-of-fit	1.11	1.11
Reflns collected	3353	5589
Unique reflns	1496	1904
Observed reflns	1356	1764
CCDC No.	959136-959138	959139-959141

S8. Results of variable temperature study performed on 4-chlorobenzoic acid and 2,3,5-trichlorosalicylic acid.

		4-Chlorobenzoic acid	2,3,5-trichlorosalicylic acid
-123 °C	Type I Cl···Cl	3.4095(8)	
	Type II Cl···Cl		3.473(1)
	Cell Volume	331.031	834.146
-73 °C	Type I Cl···Cl	3.4186(8)	
	% increase	0.27%	
	Type II Cl···Cl		3.498(1)
	% increase		0.72%
	Cell Volume	333.631	843.821
	% increase	0.79%	1.16%
23°C	Type I Cl···Cl	3.448(1)	
	% increase	1.13%	
	Type II Cl···Cl		3.547(1)
	% increase		2.13%
	Cell Volume	341.16	855.868
	% increase	3.05%	2.6%