

“Symthons show how fluorine disrupts π - π stacking in halobenzenes”.

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S1: Melting Points of Unmixed Halobenzenes.

Table S1.1: Melting Point Data (°C).

isomer	N	Fluorine	Chlorine	Bromine	Iodine
0	0				5
1	1	-42	-46	-31	-31
1,2	2	-34	-18	6	27
1,3	2	-59	-25	-7	37
1,4	2	-13	53	87	131
1,2,3	3		54	88	116
1,2,4	3		17	43	
1,3,5	3	-6	64	123	184
1,2,3,4	4	-42	47		136
1,2,4,5	4	4	140	180	254
1,2,3,5	4	-48	54	100	148
1,2,3,4,5	5	-48	86	161	172
1,2,3,4,5,6	6	4	230	327	

Experimental Data from reference 22: J-C. Bradley, A. Williams & A. Lang, "[Jean-Claude Bradley Open Melting Point Dataset](#)" (2014). Centrosymmetric molecules in bold type. The data (iodobenzenes excepted) are shown in graphical form for non-centrosymmetric and centrosymmetric molecules in Figure S1.1 below. All fluorobenzenes have sub-ambient melting temperatures. Chlorobenzenes and Bromobenzenes show gradual increases in melting temperature with increasing number of halogen substituents, N.

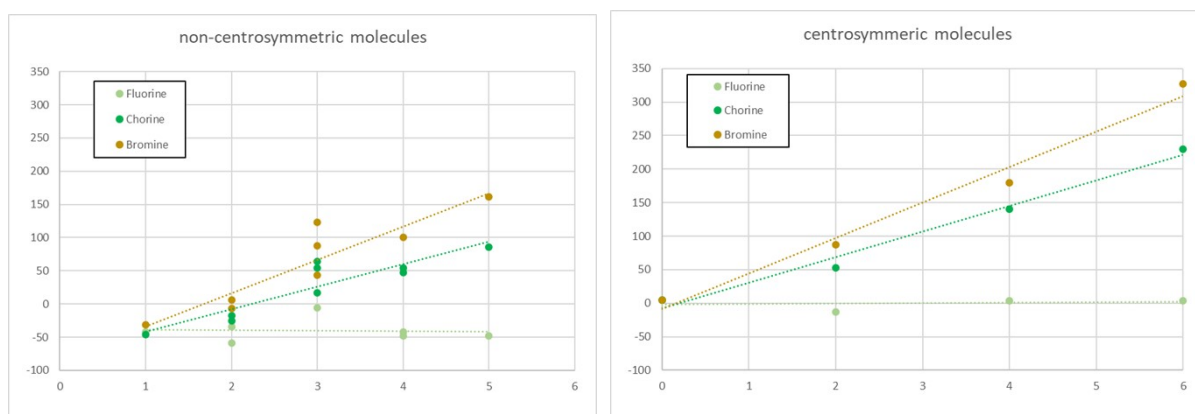


Fig. S1.1: Melting Points of unmixed fluoro-, chlor- and bromobenzenes, as a function of number of halogen substituents, N. Data for non-centrosymmetric molecules (N = 1-5) on the left and for centrosymmetric molecules (N always even) on the right.

S2: Fluorobenzene crystal structures.

Table S2: Crystal Structures of Fluorobenzenes

Fluorobenzenes													
N	halogen positions						CSD REFCODE	Space Group	Z'	k	Short axis	Short repeat (Å)	Symmetry of short repeat
	1	2	3	4	5	6							
1	F						FACFAQ	P4321	1	1	a	5.8	2 x Symthon II
2	F	F					FACFOE	P21/n	1	1	b	5.96	2 x Symthon II
2	F		F				PUGDAX	C2/c	2	2	c	7.23	2 x Symthon II
2	F			F			FACGEV	P21/c	0.5	1	b	6.53	2 x Symthon II
3	F		F		F		PVVAWA01	I2/a	1	1	c	7.504	2 x Symthon III
3	F	F	F				PUGDEB	C2/c	1	1	c	7.05	2 x Symthon III
4	F	F	F		F		CUWYUP	P21/c	1	1	a	3.7	Symthon I
4	F	F		F	F		FACJAU		0.5	1	a	4.47	offset translation
4	F	F	F	F			ZELDOJ	P21/n	1	1	b	7.56	2 x halogen edge
4	F	F	F	F			ZELDOJ01	C2/c	1	1	b	6.95	other
5	F	F	F	F	F		FACMOL	P21/c	2	2	b	9.88	2 x halogen edge
6	F	F	F	F	F	F	HF BENZ02	P21/n	1.5	2	a	5.9	other
6	F	F	F	F	F	F	HF BENZ15	C2/c	0.5	1	b	7.383	other

Notes: There are crystal structures for eleven of the twelve possible fluorobenzene molecules – only 1,2,4-trifluorobenzene is not represented. Two fluorobenzenes show polymorphism, giving a total of thirteen crystal structures. Three of these structures have two molecules in the asymmetric unit, giving sixteen crystallographically independent aromatic rings, each with two sites (one above each ring, one below it) for close aromatic approaches.

S3: Crystal Explorer Calculations

Table S3.1: Interaction Energies in Fluorobenzenes, in kJ/mol.

				hollow 1		hollow2		next
0		BENZEN		-9.7	SI	-9.7	SI	-6.1
1		FACFAQ		-10.3	SI	-10.3	SI	-6.6
2	1,2	FACFOE		-13.9	SI	-11.4	SI	-10.3
2	1,3	PUGDAX	blue	-12.1	SI	-11.5	'SI'	-7.7
2		PUGDAX	green	-11.4	'SI'	-11.1	SI	-7.7
2	1,4	FACGEV		-10.9	SI	-10.9	SI	-8.2
3	1,2,3	PUGDEB		-22.6	SII	-22.6	SII	-8.2
3	1,2,4							
3	1,3,5	PVAWA01		-17.2	SII	-17.2	SII	-8.5
4	1,2,4,5	FACJAU		-15.6	offset	-15.6	offset	-8.7
4	1,2,3,5	CUWYUP		-17.5	SI	-17.5	SI	-7.9
4	1,2,3,4	ZELDOJ		-23	SII	-10.7	hal edge	-10.3
5	1,2,3,4,5	FACMOL	blue	-22.2	SII	-8.9	hal edge	-10.8
5		FACMOL	green	-22.1	SII	-10.3	hal edge	-9.4
6		HFBNZ02	blue	-11.4	hal edge	-11.4	hal edge	-12.5
6		HFBNZ02	green	-12.1	hal edge	-7.4	hal 'T'	-13

Data in red indicate the five closest approaches which are not the strongest interactions: four in HFBNZ02 and one in FACMOL. Further details are given in S13.

Table S3.2: Interaction Energies in Chlorobenzenes, in kJ/mol.

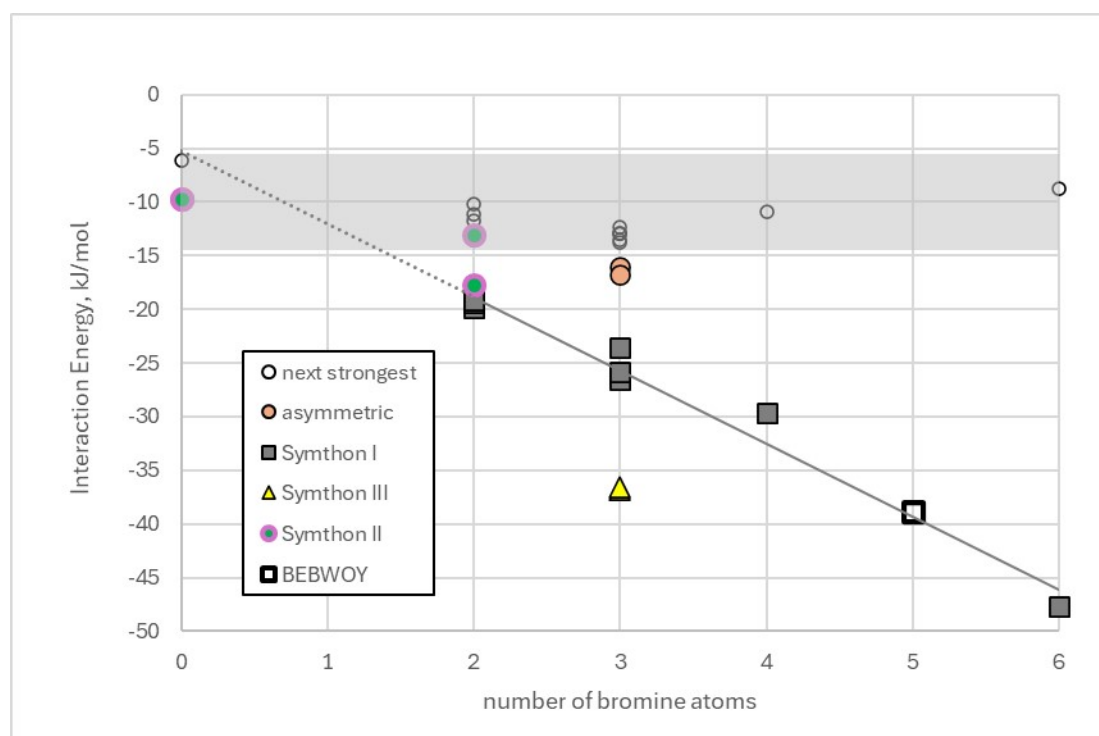
				1st		2nd		next
0		BENZEN		-9.7	SI	-9.7	SI	-6.1
1		MCBENZ03		-13.5	SI	-10.7	SI	-8.6
2	1,2	ABUMIT01		-16.5	SI	-16.5	SI	-9.3
2	1,3	ABUMOZ	blue	-16.7	SI	-16.7	SI	-8.3
2		ABUMOZ	green	-16.2	SI	-16.2	SI	-10.3
2	1,4	DCLBEN01		-16.4	SI	-16.4	SI	-10.8
3	1,2,3	TCBENZ	blue	-29.8	SII	-10.2	hal edge	-11.4
3		TCBENZ	green	-30.4	SII	-10.8	hal edge	-12
3	1,2,4	KUBMAX	blue	-19.9	SI	-19.9	SI	-9
3		KUBMAX	green	-21.2	SI	-21.2	SI	-9
3	1,3,5	TCHLBZ		-21.1	SI	-21.1	SI	-9
4	1,2,4,5	TCLBEN02		-24	SI	-24	SI	-8.7
4	1,2,3,5	TCLBZN	blue	-23.6	SI	-23.6	SI	-8.7
4		TCLBZN	green	-24.4	SI	-24.4	SI	-8.7
4	1,2,3,4	NILJOK		-24.1	SI	-24.1	SI	-8.1
5		PNCLBZ		-28	SI	-28	SI	-9.2
6		HCLBNZ11		-33.3	SI	-33.3	SI	-5.1

Data in red indicate the two closest approaches which are not the strongest interactions, both in TCBENZ. Further details are given in S13.

Table S3.3: Interaction Energies in Bromobenzenes, in kJ/mol.

			1st		2nd		
0	BENZEN		-9.7	SI	-9.7	SI	-6.1
1							
2	1,2	SOFWIV	-17.7	SI	-13.1	SI	-11.7
2	1,3	SOFVUG	blue	-19.4	SI	-19.4	SI
2		SOFVUG	green	-19.2	SI	-19.2	SI
2	1,4	CISTON02		-19.9	SI	-19.9	SI
3	1,2,3	UYUPIQ	blue	-36.8	SII	-16.1	hal edge
3		UYUPIQ	green	-36.6	SII	-16.8	hal edge
3	1,2,4	UYUQAJ	blue	-26.2	SI	-26.2	SI
3		UYUQAJ	green	-23.6	SI	-23.6	SI
3		UYUQAJ	red	-26.5	SI	-26.5	SI
3	1,3,5	TBRMBZ		-25.8	SI	-25.8	SI
4	1,2,4,5	TETBZ06		-29.6	SI	-29.6	SI
4	1,2,3,5						
4	1,2,3,4						
5		BEBWOY					
6		HBRBEN02		-47.7	SI	-47.7	SI

Fig S3.1 Strength of Interactions in bromobenzenes, in kJ/mol.



This plot is in the same format as equivalent plots for fluorobenzenes and chlorobenzenes in Figure 4 of the main paper. The plot is broadly similar to that for chlorobenzenes, although Symthon I interactions are stronger. The straight line is a linear fit for Symthon I interactions, with $y = -5.2483 - 6.8095N$. This gives a predicted interaction energy of -39.3 kJ/mol for Symthon I in C_6HBr_5 . This is consistent with the energy calculated from the crystal structure of BEBWOY of -38.8 kJ/mol.

S4: Crystal Structures of other halobenzenes with fluorine

N	halogen positions						CSD REFCODE	Space Group	Z'	k	Short axis	Short repeat (Å)	Symmetry of short repeat
	1	2	3	4	5	6							
2	Cl	F					NAFCUV	Pbca	1	1	a	5.907	other
2	Br	F					NAFDOQ	P21/n	1	1	a	5.97	other
2	F	I					NAFFEI	P21/c	1	1	a	4.447	offset translation
2	Cl		F				NAFDAC	P21/c	1	1	b	4.931	offset translation
2	Br		F				NAFDUW	Pna21	2	2	b	3.977	Symthon I
2	F		I				NAFFIM	P21	5	5	b	4.275	Symthon I
2	Cl			F			FACPAA01	P21/n	3	3	b	6.023	2 x Symthon II
2	Br			F			FACQAB01	P21/n	3	3	b	6.137	2 x Symthon II
2	F			I			FACQEF01	Pnma	1	1	c	4.893	offset translation
4	F		Br	Cl	Br		SOXLEX01	P21/c	1	1	a	3.894	Symthon I
4	F	Br	F		F		XAJNUT	Pc	1	1	a	3.957	Symthon I
4	F	Br	F		F		XAJNUT02	P21	1	1	a	4.107	Symthon I
4	I	I	I		F		SIXPEW	Ibca	1	2	a	8.853	2 x offset inversion
6	F	F	F	F	F	I	ZAHGAQ01	P21/c	2	2	c	9.121	2 x halogen edge
6	F	F	F	F	F	I	ZAHGAQ	P21/c	1	1	a	10.556	2 x offset inversion
6	Cl	F	F	I	F	F	GEHMIT	P21/c	0.5	1	a	5.86	offset translation
6	Br	F	F	I	F	F	GEHMEP	C2/m	0.25	1	c	5.223	offset translation
6	F	F	I	F	F	I	ZZZAVM02	P21/c	0.5	1	c	5.788	offset translation
6	F	F	Br	F	F	Br	ZZZAVJ01	P21/c	0.5	1	c	5.353	offset translation
6	F	F	F	F	I	I	WISBOR	P21/n	1	1	b	5.77	offset translation
6	F	F	F	Br	F	Br	PASKUR	P21/c	1	1	c	5.162	offset translation
6	F	F	I	F	F	I	ZZZAVM01	P21/c	0.5	1	b	6.069	2 x halogen edge
6	F	I	F	I	F	I	UCEPEY	P21/n	1	1	b	4.793	offset translation
6	F	I	F	I	F	I	UCEPEY02	P21/c	1	1	c	9.219	2 x halogen edge
6	F	Cl	F	Cl	F	Cl	BARBOL	P63/m	0.167	1	c	6.282	other
6	F	F	I	I	I	I	PERDAT	I41/a	1	1	c	9.744	2 x halogen edge
6	F	I	F	I	I	I	PEYAU	P21	1	1	b	4.332	Symthon I
6	F	I	I	F	I	I	PERCUM	P21/n	0.5	1	b	5.239	offset translation
6	F	I	I	I	I	I	PERCOG	P-1	2	2	a	8.526	2 x Symthon III

Notes: There were crystal structures for 25 halofluorobenzenes, including all nine di-substituted molecules (N=2), three tetra halofluorobenzenes (N=4) and thirteen fully substituted halofluorobenzenes (N=6). Four of these compounds are polymorphic, giving 29 crystal structures in all. The crystal structure NAFFIM has Z'=5, two crystal structures (FACPAA01 and FACQAB01) have Z'=3 and a further four have two molecules in the asymmetric unit, giving a total of 41 crystallographically independent aromatic rings, each with two sites for close approaches. Thus the full 'with fluorine' dataset of both fluorobenzene and halofluorobenzene crystal structures contains 114 (= 32 + 82) sites for close aromatic approaches. The four crystal structures each having one shorter repeat that is not included in this table are FACGEV, PVVAWA01, ZELDOJ and ZAHGAQ.

S5: Symmetries of closest approaches on each face in halobenzenes containing fluorine

N	isomer	Fluorobenzenes	Halofluorobenzenes in order (left to right) of decreasing fluorine content							
1		FACFAQ								
	1,2	FACFOE	NAF CUV	NAF DOQ	NAF FEI					
2	1,4	FAC GEV	FAC PAA O1	FAC QAB O1	FACQ EF01					
	1,3	PUG DAX	NAF DAC	NAF DUW	N A F FI M					
3	1,3,5	PVVA WA01								
	1,2,4									
	1,2,3	PUG DEB								
4	1,2,3,5	CUW YUP 4 F	XA NUT 3 F	XAJN UT02 3 F	SOXLEX01 1 F	SIX PEW 1 F				
	1,2,4,5	FAC JAU								
5		ZEL DOJ								
	1,2,3,4	ZELD OJ01								
6		HFBE NZ02 6 F	ZAHG AQ01 5 F	GEH MIT 4 F	ZZA VM02 4 F	WIS BOR 4 F	ZZZAVM01 4 F	UCEPEY02 3 F	PERDAT 2 F	PER COG 1 F
		HFBE NZ15 6 F	ZAH GAQ 5 F	GEH MEP 4 F	ZZA VJ01 4 F	PAS KUR 4 F	UCEPEY 3 F	BARBOL 3 F	PERCUM 2 F	PEX YAU 2 F

Fig. S5.1: Symmetries of approaches on each face in halobenzenes containing fluorine.

Key:	face...face	translation	inversion	skewed
	edge...face	screw	glide	asymmetric

Numbers of fluorine substituents are shown for 1,2,3,5-tetrahalobenzenes and for N = 6. The symmetries embodied in the closest approaches on each aromatic face in all 42 crystal structures are displayed. Each coloured cell represents the symmetry embodied in the closest approach on one aromatic face. Most crystal structures have one molecule in the asymmetric unit, so their closest approaches are paired, with the REFCODE given in the upper cell. For example, the crystal structure of 1,2-difluorobenzene (FACFOE) is represented by two green cells for the two closest approaches, one on each face of the aromatic ring. Both these approaches embody glide symmetry. Similarly, the closest approach on one face of the aromatic ring of 1-fluoro-4-iodobenzene in FACQEF01 embodies translation symmetry and is paired with a related approach on the other face; this is represented as a pair of grey cells.

For the ten crystal structures with more than one molecule in the asymmetric unit, the cells have been split and coloured according to their individual symmetries. Close approaches occurring within the asymmetric unit do not embody symmetry; they are classified as 'asymmetric' and coloured orange. In this dataset, all the asymmetric approaches are edge...face. For example, HFBENZ02 has two C₆F₆ molecules in the asymmetric unit, represented by four cells. Three of these approaches are asymmetric and one embodies screw symmetry - represented by one green cell and three orange cells. All four approaches are edge...face.

For 1,2,3,5-tetrafluorobenzenes and N = 6 the number of fluorine atoms in each molecule is also shown in the lower cells for each crystal structure – with fluorine content decreasing from left to right. Close approaches are usually paired with approaches of the same symmetry. The most common exceptions are screw/glide, screw/inversion and glide/inversion pairings, each of which occurs three times. The fifteen asymmetric approaches occur in five crystal structures, always accompanied by at least one symmetric approach.

S6: Geometries of face...face approaches embodying translation

CSD REFCODE	©...© Å	s Å	d Å	©...X Å	X	classification
FACJAU	4.472	3.297	3.021	3.307	F	offset translation
FACJAU	4.472	3.297	3.021	3.307	F	offset translation
NAFFEI	4.447	3.513	2.727	3.491	F	offset translation
NAFFEI	4.447	3.513	2.727	3.757	C	offset translation
FACQEF01	4.893	3.722	3.176	3.744	I	offset translation
FACQEF01	4.893	3.722	3.176	3.744	F	offset translation
NAFDUW	3.977	3.481	1.923	3.516	C	Symthon I
NAFDUW	3.977	3.481	1.923	3.531	C	Symthon I
NAFDUW	3.977	3.442	1.992	3.501	C	Symthon I
NAFDUW	3.977	3.442	1.992	3.505	C	Symthon I
NAFDAC	4.931	3.469	3.504	3.539	CI	offset translation
NAFFIM	4.275	3.364	2.638	3.685	C	Symthon I
NAFFIM	4.275	3.364	2.638	3.387	F	Symthon I
NAFFIM	4.275	3.386	2.61	3.602	C	Symthon I
NAFFIM	4.275	3.386	2.61	3.391	F	Symthon I
NAFFIM	4.275	3.468	2.5	3.705	C	Symthon I
NAFFIM	4.275	3.468	2.5	3.696	C	Symthon I
NAFFIM	4.275	3.528	2.414	3.669	C	Symthon I
NAFFIM	4.275	3.528	2.414	3.587	F	Symthon I
NAFFIM	4.275	3.576	2.343	3.636	C	Symthon I
NAFFIM	4.275	3.576	2.343	3.42	F	Symthon I
CUWYUP	3.703	3.442	1.366	3.442	C	Symthon I
CUWYUP	3.703	3.442	1.366	3.447	C	Symthon I
SOXLEX01	3.894	3.561	1.576	3.582	C	Symthon I
SOXLEX01	3.894	3.561	1.576	3.588	C	Symthon I
XAJNUT	3.957	3.508	1.831	3.552	C	Symthon I
XAJNUT	3.957	3.508	1.831	3.552	C	Symthon I
XAJNUT02	4.107	3.532	2.096	3.616	C	Symthon I
XAJNUT02	4.107	3.532	2.096	3.58	F	Symthon I
PEXYAU	4.332	3.687	2.274	3.826	C	Symthon I
PEXYAU	4.332	3.687	2.274	3.689	F	Symthon I
PASKUR	5.162	3.488	3.805	3.604	Br	offset translation
PASKUR	5.162	3.488	3.805	3.662	F	offset translation
UCEPEY	4.793	3.604	3.16	3.684	F	offset translation
UCEPEY	4.793	3.604	3.16	3.728	I	offset translation
WISBOR	5.66	3.583	4.382	4.158	I	offset translation
ZZZAVM02	5.788	3.895	4.281	3.954	I	offset translation
ZZZAVM02	5.788	3.895	4.281	3.954	I	offset translation
ZZZAVJ01	5.353	3.665	3.902	3.738	Br	offset translation
ZZZAVJ01	5.353	3.665	3.902	3.738	Br	offset translation
PERCUM	5.239	3.72	3.689	4.014	I	offset translation
PERCUM	5.239	3.72	3.689	4.014	I	offset translation
GEHMIT	5.86	3.934	4.343	3.943	CI/I	offset translation
GEHMIT	5.86	3.934	4.343	3.943	CI/I	offset translation

Notes on translations

In addition to the three molecules shown in Figure 10 of the main paper, Symthon I also accommodates fluorine in three other molecules: 1-bromo-3-fluorobenzene (NAFDUW), 1-iodo-3-fluorobenzene (NAFFIM) and 1,3-difluoro-2,4,5,6-tetraiodobenzene (PEXYAU).

The other approaches with larger displacements ($d > 2.7\text{\AA}$) were inspected to see which atoms occupied these hollows. Nine were occupied by iodine, six by fluorine, four by bromine and three by chlorine atoms. Interpretation of these data requires comparison with the number of times these atoms *could* occupy hollows, based on which halogen substituents are present. Iodine occupies hollows in nine out of ten approaches in which it is present. Chlorine and bromine occupy hollows each time they are present. Fluorine atoms are accessible for 18 hollows, yet they only occupy six of them - in five of which no other halogen atom is available.

Three non-centrosymmetric molecules adopt offset translations: NAFFEI, NAFDAC, PASKUR, WISBOR and UCEPEY. In these examples it is also the heavier halogen atom that occupies hollows, subject to the constraint of para-substitution to give offset stacks.

XAJNUT and XAJNUT02 contain symthon I stacks with subtly different displacements; this source of $Z' > 1$ and polymorphism was noted previously in halobenzenes without fluorine

S7: Geometries of face...face approaches embodying inversion

CSD REFCODE	©...© Å	s Å	d Å	©...X Å	X	classification
PVVAWA01	3.754	3.466	1.442	3.519	C	symthon III
PVVAWA01	3.754	3.466	1.442	3.519	C	symthon III
PUGDEB	3.636	3.494	1.006	3.55	C	symthon III
PUGDEB	3.636	3.494	1.006	3.55	C	symthon III
ZELDOJ	3.628	3.35	1.393	3.41	C	symthon III
FACMOL	3.642	3.354	1.419	3.38	C	symthon III
FACMOL	3.604	3.363	1.296	3.38	C	symthon III
ZELDOJ01	4.282	3.346	2.672	3.32	F	symthon III
NAFDOQ	3.849	3.469	1.668	3.489	C	symthon III
NAFDAC	4.723	3.31	3.369	3.74	F	offset inversion
FACPA01	3.78	3.49	1.452	3.551	C	symthon III
FACQAB01	3.875	3.554	1.544	3.621	C	symthon III
SIXPEW	4.86	3.613	3.251	3.745	I	offset inversion
SIXPEW	4.86	3.613	3.251	3.745	I	offset inversion
SIXPEW	5.089	3.878	3.295	4.057	I	offset inversion
SIXPEW	5.089	3.878	3.295	4.057	I	offset inversion
PERCOG	4.28	3.737	2.086	3.852	C	symthon III
PERCOG	4.257	3.7	2.105	3.784	C	symthon III
PERCOG	4.245	3.739	2.01	3.837	C	symthon III
PERCOG	4.291	3.669	2.225	3.788	C	symthon III
PERDAT	3.925	3.615	1.529	3.54	F	symthon III
UCEPEY02	3.858	3.53	1.557	3.577	C	symthon III
ZAHGAQ	6.035	4.148	4.384	4.146	I	offset inversion
ZAHGAQ	4.523	3.259	3.136	3.307	F	offset inversion

Notes on inversions

The molecules in PUGDEB, PVVAWA01 and SIXPEW ($Z'=2$) all lie on 2-fold rotation axes, so the inversion approaches are pairs with identical geometries. The smallest displacement, (d) = 1.006Å for 1,2,3-trifluorobenzene in PUGDEB is consistent with similar displacements in six 1,2,3-trihalobenzenes without fluorine.⁵ These allow favourable connections between carbon atoms carrying opposing charges. It seems likely that the (as yet undetermined) crystal structures of other 1,2,3-trihalobenzenes with fluorine will show similar close approaches. Symthon III approaches are paired in PUGDEB, as well as in 1,3,5-trifluorobenzene (PVVAWA01) and C_6F_5 in PERCOG ($Z'=2$) resulting in a variant of π - π stacking in which every second molecule is related by translation. The remaining seven inversion approaches are 'offset inversions' – as shown schematically in Fig. 1f. Six of these offset inversions are paired in 1-fluoro-3,4,5-triodobenzene (SIXPEW, $Z'=2$) and one polymorph of C_6HF_5 (ZAHGAQ); every second molecule is again related by translation. One of the interplanar spacings in ZAHGAQ, (s) = 3.259Å, is unusually small and the other, (s) = 4.148Å, is unusually large and was omitted from Fig. 7. There may be a third polymorph of C_6HF_5 with more typical interplanar spacings. The remaining offset inversion occurs for 1-chloro-3-fluorobenzene (NAFDAC).

S8: Symmetries and Geometries of Edge...Face Approaches

CSD REFCODE	©...C Å	C...C Å	©...X Å	X	other edge	geometry <i>italics symmetric</i>
FACFAQ	3.57	3.726		C	C	symthon II
FACFAQ	3.57	3.726		C	C	symthon II
FACFOE	3.483	3.632		C	C	symthon II
FACFOE	3.676	3.826		C	F	symthon II
PUGDAX	3.515	3.677		C	C	symthon II
PUGDAX	3.528	3.703		C	C	<i>symthon II</i>
PUGDAX	3.665	3.81		C	F	<i>symthon II</i>
PUGDAX	3.655	3.79		C	F	symthon II
FACGEV	3.72	3.799		C	F	symthon II
FACGEV	3.72	3.799		C	F	symthon II
ZELDOJ	4.329	4.221	3.391	F	F	Fluorine edge
FACMOL	4.457	4.458	3.538	F	F	Fluorine edge
FACMOL	4.441	4.063	3.566	F	F	Fluorine edge
HFBNZO2	4.201	4.015	3.152	F	F	<i>Fluorine edge</i>
HFBNZO2	4.523	5.121	3.29	F		distorted
HFBNZO2	4.317	3.91	3.399	F	F	<i>Fluorine edge</i>
HFBNZO2	4.317	3.91	3.399	F	F	<i>Fluorine edge</i>
FACPAA01	3.54	3.78		C	F	<i>symthon II</i>
FACPAA01	3.53	3.935		C	Cl	<i>symthon II</i>
FACPAA01	3.525	4.077		C	Cl	<i>symthon II</i>
FACPAA01	3.554	3.846		C	F	<i>symthon II</i>
FACPAA01	3.493	3.983		C	F	symthon II
FACQAB01	3.599	3.976		C	F	<i>symthon II</i>
FACQAB01	3.597	4		C	Br	<i>symthon II</i>
FACQAB01	3.58	4.011		C	Br	<i>symthon II</i>
FACQAB01	3.626	3.88		C	F	<i>symthon II</i>
FACQAB01	3.593	3.936		C	F	symthon II
NAFCUV	3.6	4.171		C		distorted
NAFCUV	3.978	3.621		C		distorted
NAFDOQ	5.203	5.618	3.531	Br		distorted
ZAHGAQ01	4.358	4.76	3.247	F	I	Fluorine edge
ZAHGAQ01	4.991	4.222	4.057	I	F	distorted
ZAHGAQ01	4.387	4.237	3.436	F	F	<i>Fluorine edge</i>
ZAHGAQ01	4.329	4.55	3.273	F	F	Fluorine edge
ZZZAVM01	4.382	4.869	3.413	F	I	Fluorine edge
ZZZAVM01	4.382	4.869	3.413	F	I	Fluorine edge
WISBOR	4.216	4.112	3.267	F	F	Fluorine edge
UCEPEY02	4.586	4.279	3.62	F	I	Fluorine edge
PERDAT	4.62	4.433	3.54	F	F	Fluorine edge

Colour code for symmetries: green = screw, magenta = glide, orange = asymmetric. ©...X distances are given where the closest heavy atom (X) to the centroid © is not a carbon atom.

S9: Isostructures

Molecule	REFCODE	SG	Z'	<i>a</i>	<i>b</i>	<i>c</i>	β
1-Cl, 4-F	FACPAA01	P2 ₁ /n	3	14.254	6.023	20.302	100.855
1-Br, 4-F	FACQAB01	P2 ₁ /n	3	14.443	6.137	20.778	101.257
1,2,4,5-F; 3,6-Br	ZZZAVJ01	P2 ₁ /c	0.5	6.042	11.368	5.353	93.10
1,2,4,5-F; 3,6-I	ZZZAVM02	P2 ₁ /c	0.5	6.219	11.617	5.788	93.61

FACPAA01 and FACQAB01 both contain one pair of asymmetric edge...face approaches, one Symthon III paired with an asymmetric edge...face approach, and one Symthon II paired with an edge...face approach, as shown in Fig. S1 above. As noted in the main text, it is likely that simpler polymorphs based on Symthon II or Symthon III pairs exist for both molecules.

ZZZAVJ01 and ZZZAVM02 both contain a pair of offset translations – see Table 5 in the main text.

S10: The fourteen unusual close approaches, not represented in Fig. 1 in the main paper.

Table S9.1: The 'unusual' close approaches

isomer	molecule	crystal structure	number of interactions	symmetry	& brief description
1,2-	C ₆ H ₄ FCI	NAFCUV	1	screw	distorted edge...face
1,2-	C ₆ H ₄ FCI	NAFCUV	1	glide	distorted edge...face
1,2-	C ₆ H ₄ FBr	NAFDOQ	1	glide	bromine T edge...face
1,2,3,4-	C ₆ H ₂ F ₄	ZELDOJ01	1	rotation	skew
1,3,5-	C ₆ F ₃ Cl ₃	BARBOL	2	inversion	edge...edge
	C ₆ HF ₅	ZAHGAQ01	1	asymmetric	distorted edge...face
	C ₆ HF ₅	ZAHGAQ01	1	asymmetric	fluorine edge...face
	C ₆ F ₆	HF BENZ02	1	screw	fluorine T edge...face
	C ₆ F ₆	HF BENZ02	3	asymmetric	fluorine edge...face
	C ₆ F ₆	HF BENZ15	2	rotation	skew

Images of Unusual Approaches, with notes:

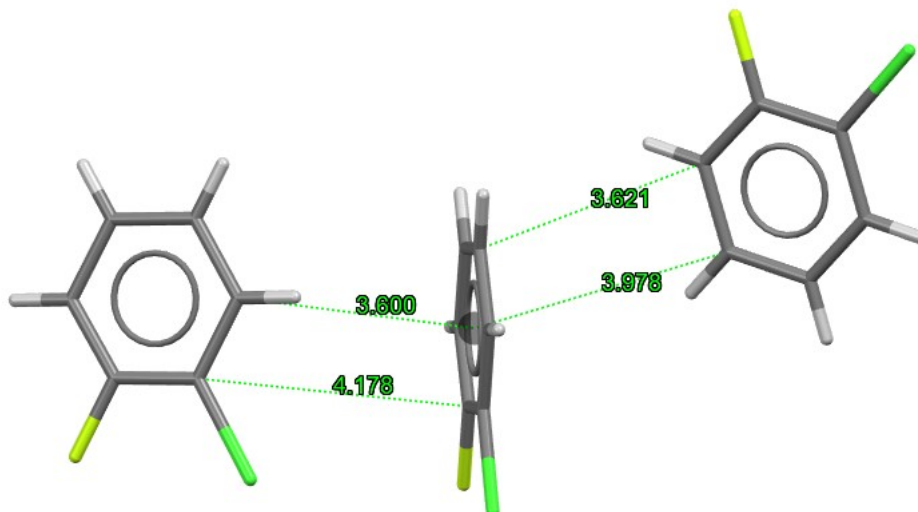


Fig. S10.1: NAFCUV: distorted edge...face geometries on each face. The approach on the right involves an edge chlorine atom.

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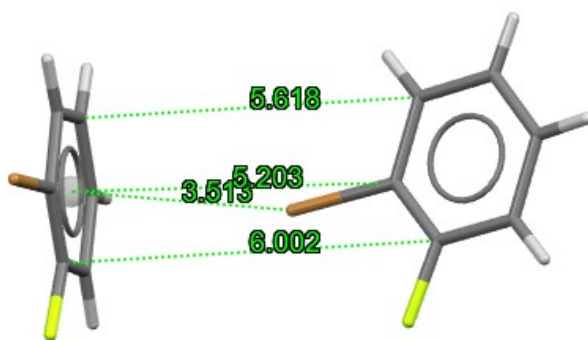


Fig. S10.2: NAFDOQ: Bromine 'T' geometry – distorted edge...face

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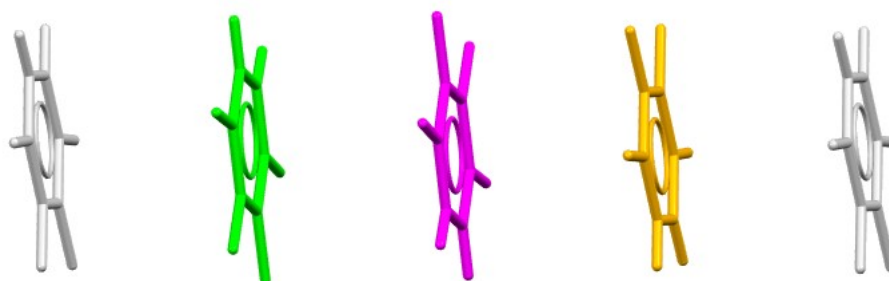


Fig. S10.3: ZELDOJ01 - Unusual π - π stack in which every 4th molecule is related by translation. The other symmetry operations are, from left to right, 2-fold rotation, inversion, 2-fold rotation, inversion. The aromatic rings related by 2-fold inversion are 'skew' – not exactly parallel.

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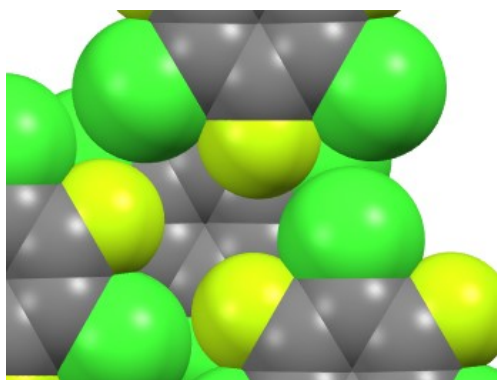


Fig. S10.4: BARBOL - The hollows above (and below) each aromatic ring are unoccupied, as shown in the figure, making this the only crystal structure in this dataset with no edge...face or face...face close aromatic approaches. This arrangement embodies the 6-fold rotoinversion axis perpendicular to the centroid, with six equal short C...F connections of 3.969Å (three on each face). The interplanar separation, (s) = 3.141Å and a displacement, (d) = 4.932 are respectively smaller and larger than those associated with π - π stacking. This approach is better described as an 'edge...edge' approach. Similar edge...edge approaches were identified previously (Black 2023) in other hexahalobenzenes and in dihalobenzenes, in association with symthon I. In BARBOL this approach occurs in the absence of any symthons; unusually it has a multiplicity of six, with replication generating the entire three-dimensional crystal structure.

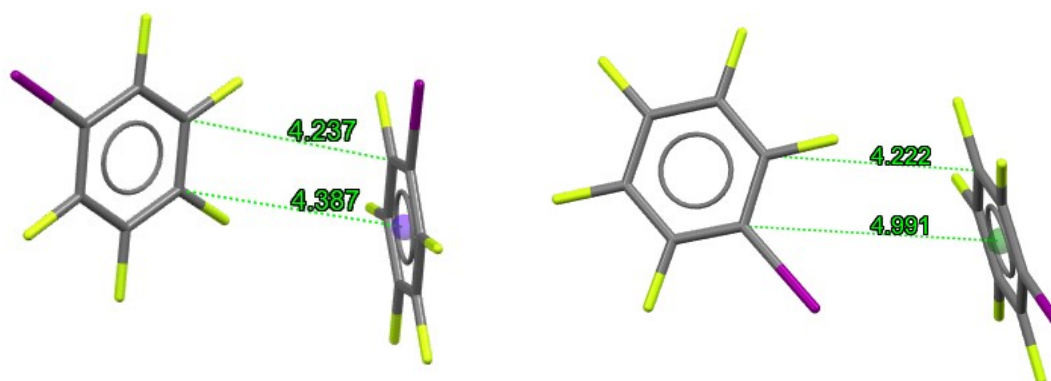


Fig. S10.5: ZAHGAQ01 ($Z'=2$) - Asymmetric fluorine edge...face on the left. Distorted asymmetric edge...face approach on the right - this distortion is due to the 'edge' iodine atom occupying the hollow. Both approaches are paired with fluorine edge...face approaches (not shown) that embody glide symmetry.



Fig. S10.6: HFBENZ15 - Unusual π - π stack in which every second C_6F_6 molecule is related by $c = 8.449\text{\AA}$ – the horizontal direction in the image. The molecular plane of the central molecule is not quite parallel to its neighbours in the stack, and the C-C and C-F bonds are not parallel. The molecules occupy inversion centres and are coloured by symmetry operator. Each approach embodies 2-fold rotational symmetry. Similar skew approaches were noted previously for one polymorph (TERLOS) of 1,2,4,5-tetraiodobenzene.

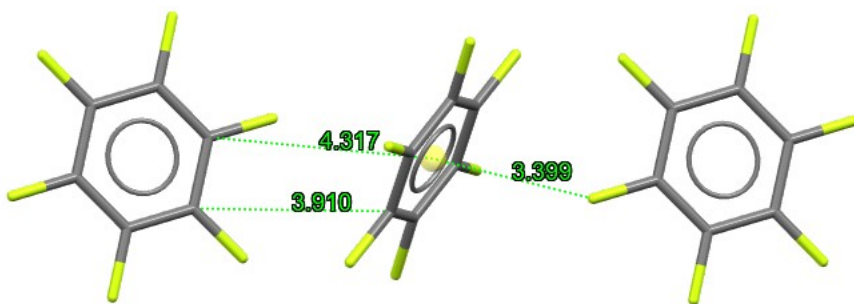


Fig. S10.7: HFBENZ02 - $Z'=2$. One 'blue' molecule occupies an inversion centre and accepts two asymmetric fluorine edge...face approaches with identical geometries, as shown above.

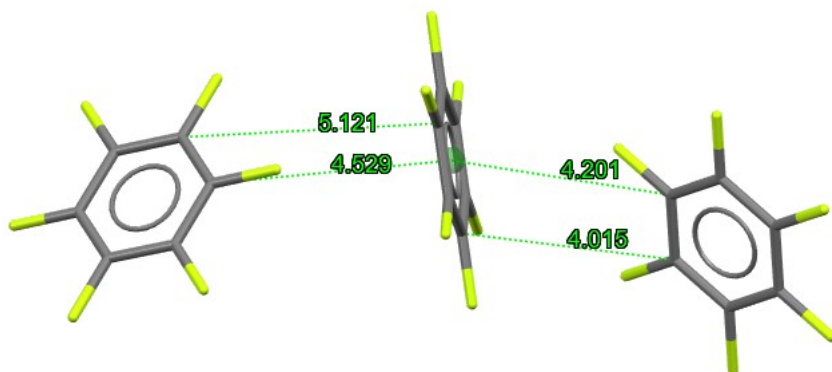


Fig. S10.8: The other ("green") molecule in HFBENZ02 does not occupy an inversion centre. There is a third asymmetric fluorine edge...face approach on the right, with $\text{C}\cdots\text{F} = 3.152\text{\AA}$. The geometry of the approach on the left is distorted so that the C-F bond points almost directly at C . This "T" approach embodies screw symmetry with $\text{C}\cdots\text{F} = 3.290\text{\AA}$. Hence all six close approaches formed as C_6F_6 crystallises are unusual.

S11: Comparison with fluorobenzene interactions in reference 21

Reference 21 in the main paper (C.J.G. Wilson, J. Plesniar, H. Kuhn, J. Armstrong, P.A. Wood, S. Parsons, *Cryst. Growth. Des.*, 2024, **24**, 2217-2225) describes close aromatic interactions in five of the fluorobenzene crystal structures included in this study.

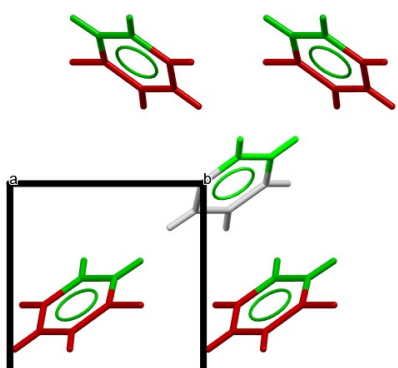
Table S11.1: Closest aromatic approaches in reference 21 and as described in this work.

Molecule	Crystal Structure REFCODE	Designation ²¹	Description in this work		
			Symthon	symmetry	multiplicity
C ₆ H ₅ F	FACFAQ	A: H... π	II	screw	4
1,2-C ₆ H ₄ F ₂	FACFOE	A: H... π	II	screw	2
		B: H... π	II	screw	2
1,4-C ₆ H ₄ F ₂	FACGEV	A: H... π	II	screw/glide	4
1,2,3-C ₆ H ₃ F ₃	PVVAWA01	A: π ... π	III	inversion	2
1,2,4,5-C ₆ H ₂ F ₄	FACJAU	A: π ... π	offset translation		2

The figures below illustrate how these Symthons and derivatives embody short crystallographic repeats in these five crystal structures. These insights are not revealed by calculated interaction energies.

FACFAQ:

2x Symthon II embodies $a = b = 5.799$



FACFOE

2x Symthon II embodies $a=7.4806$, $b = 5.9608$

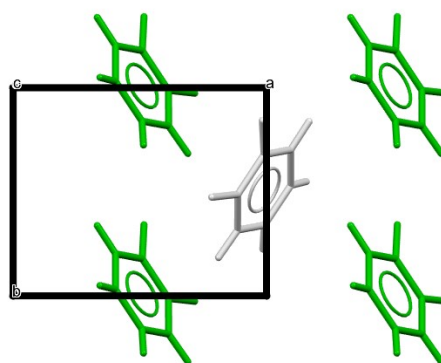


Fig. S11.1: How Symthons embody short crystallographic repeats in FACFAQ (left) and FACFOE (right)

FACGEV: 2 x Symthon II embodies $b=6.530$ and $c = 7.190$

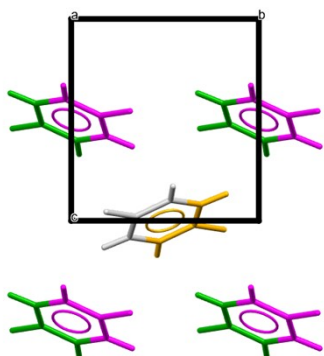


Fig. S11.2: How Symthons embody short crystallographic repeats in FACGEV

PVVAWA01: 2 x Symthon III embodies $c= 7.504$

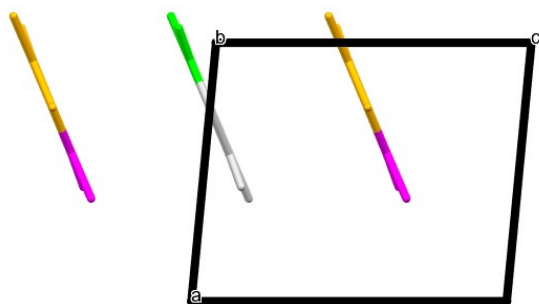


Fig. S11.3: How Symthons embody short crystallographic repeats in PVVAWA01

FACJAU: Offset translation embodies $a = 4.4719$

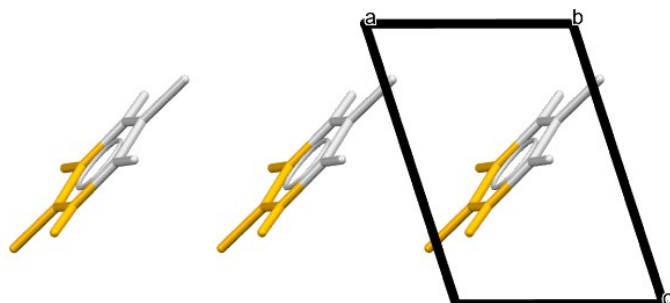


Fig. S11.4: How Symthons embody short crystallographic repeats in FACJAU

S12: NAFFIM – “just overlapping” aromatic rings.

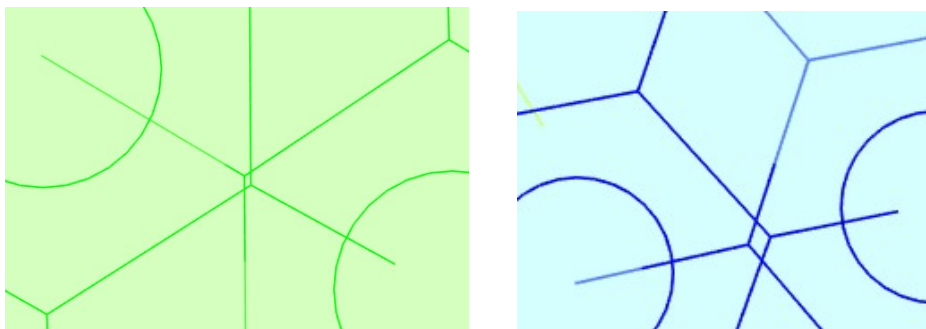


Fig. S12.1: “Just overlapping” versions of Symthon I

NAFFIM (1-fluoro-3-iodobenzene, $Z'=5$) : The two Symthon I approaches with the largest displacements: $d = 2.638\text{\AA}$ (green, left) and 2.610\AA (blue, right) are shown in Fig. S12.1. Both views are exactly parallel to the aromatic planes and the molecules are displayed in wireframe style to show that carbon atoms from one ring *just* overlap the neighbouring ring. $N=5$ for this crystal structure – the other three symthon I approaches have smaller displacements. Four of the five independent molecules displayed hydrogen/fluorine disorder at the 1 and 5 positions. As noted in the main text, it seems probable that there is a simpler polymorph of this molecule based on Symthon I with $Z'=1$.

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S13: Additional notes on FACMOL, TCBENZ and HFBENZ02

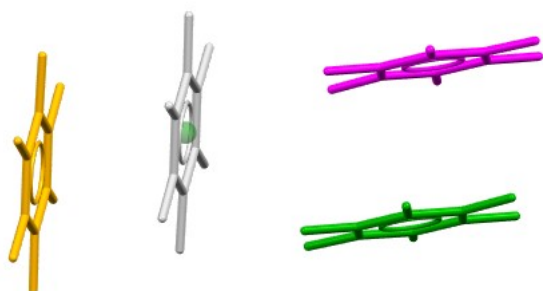


Fig. S13.1: “double fluorine edge...face” close approach in FACMOL; molecules coloured by symmetry operation.

In **FACMOL** (C_6F_5H , $Z'=2$) each molecule takes part in one symthon III inversion and one ‘double’ fluorine edge...face approach as illustrated on the left and right respectively. In a previous study¹⁰ this inversion was described as a ‘stacked centrosymmetric diad’, noting that it is also present in ZELDOJ. The ‘doubling’ of the fluorine edge arises because the green edge molecule in the figure is necessarily related to the magenta molecule by a symthon III inversion. The interaction energies of the ‘edge’ molecules with the face molecule are similar, and in one case the closer molecule has a lower interaction energy – see Table S3.1 This motif is also adopted by 1,2-difluoro-3,4,5,6-diiodobenzene in PERDAT.

A similar “double edge...face” behaviour was noted previously for 1,2,3-trihalobenzene in **TCBENZ**.² In that case the ‘double edge’ is a combination of a ‘chlorine edge...face’ interaction and a halogen-free edge...face interaction. This structure also features ‘edge...edge’ interactions which are stronger than either of the two edge...face interactions – see Table S3.2.

The strongest interaction in **HFBENZ02** is the edge...edge interaction shown in Figure S13.2. This interaction is similar to that shown for BARBOL in Figure S10.4. The two molecules are not coplanar and this is not an ‘offset translation’. The interplanar separation is 2.645\AA , with one fluorine atom in each molecule lying above/below the pocket created by an F-C=C-F edge in the neighbouring molecules. This interaction embodies the shortest unit cell repeat of $a = 5.904\text{\AA}$. As noted in Table S3.1, this interaction is stronger than all four ‘edge...face’ interactions, three of which are asymmetric and one of which has a distorted ‘T’ geometry – see Figs. S10.7 & S10.8.

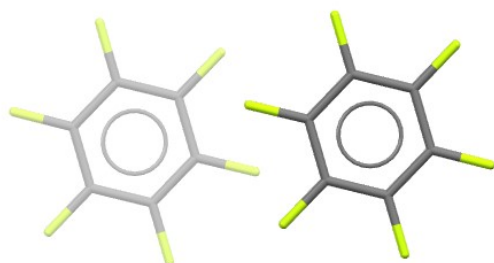


Fig. S13.2: ‘edge...edge’ interaction in HFBENZ02