Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

C–H···F–C hydrogen bonding in highly fluorinated naphthalenes

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Table S1.

Number of CSD crystal structure hits:	6,416
[1] Number of C–H···$(F–C)_2$ observations (Raw Data)	13,009
[2] Number of C–H···$(F–C)_2$ observations (Refined Data)	9,534
[3] Number of Refined C–H···$(F–C)_2$ observations with $R_{HF(a)}{}^3 \leq 1.2$	9,474
[4] Number of Refined C–H···$(F–C)_2$ observations with $R_{HF(a)}{}^3 \leq 1.15$	9,240
Average H···F_a distance / Å (for $R_{HF(a)}{}^3 \leq 1.15$)	2.564
Average H···F_b distance / Å (for $R_{HF(a)}{}^3 \leq 1.15$)	2.729

[1] Raw data correspond to data extracted in automated manner directly from the structures found via the CSD search.
[2] Refined data are those observations remaining after removal of: duplicate structures, trifurcated and multifurcated interactions, incorrectly normalized "C–H distances" (interactions typically involving deuterium), and structures with an $R(F) \leq 10$.
[3] The distance cut-off value is arbitrary. This value was chosen for graphical convenience in Figures 7 and 8.
[4] The distance cut-off value is arbitrary. This value was used in Figures 6 and 9 for ease of comparison with previous studies (refs 10b and 32b).

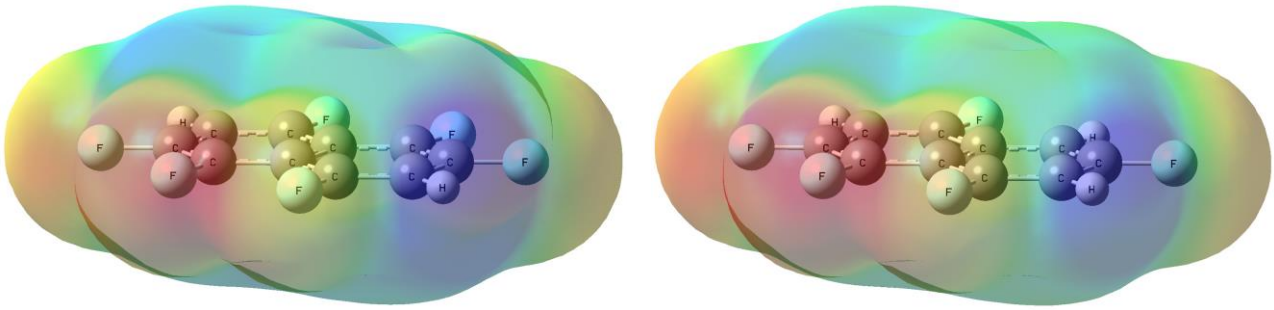

Figure S1. Electrostatic potential calculated on the ρ = 0.004 a.u. isosurface (approximately the van der Waals surface) of the molecule for (a) 1,2,4,5,6,8-hexafluoronaphthalene and (b) 1,2,4,6,8-pentafluoronaphthalene. Colours: blue (most positive), green (neutral), red (most negative). Views rotated relative to images in Figure 5.

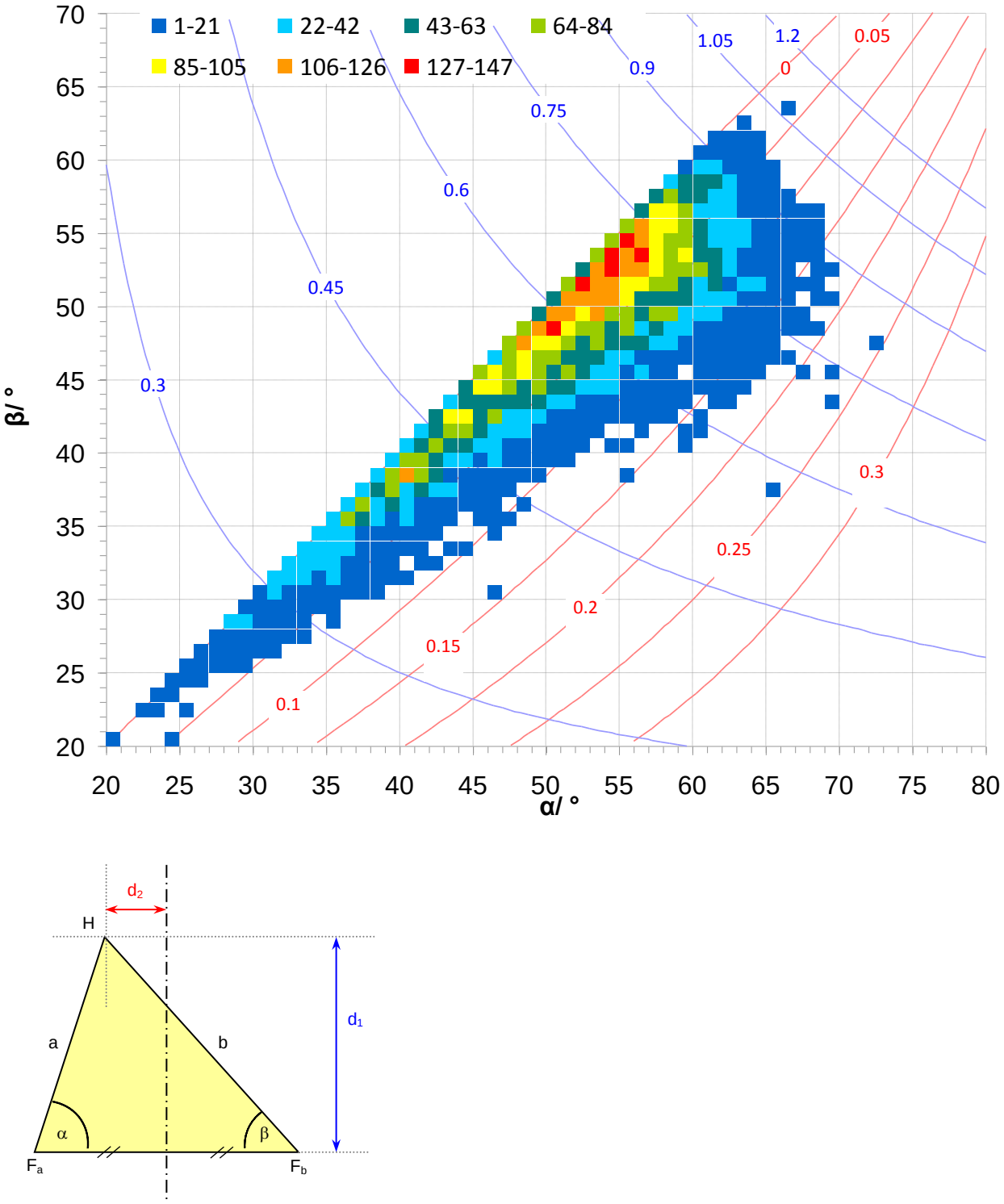

Figure S2. (Top) Asymmetry of C–H···(F–C)$_2$ bifurcated hydrogen bonds expressed in terms of location of H-atom relative to the two F-atoms (i.e. the positions of all three carbon atoms are ignored). This is expressed as a scattergram of the two H···F···F angles associated with each bifurcated hydrogen bond, and contoured by number of observations. The larger H···F···F angle (α) of the two corresponds to the horizontal axis and the smaller angle (β) to the vertical axis. Isovalues for d_1 and d_2 are shown in red and blue, respectively. **(Bottom)** Schematic of H-atom position relative to two F-atom positions showing definition of distances and angles used in assessment of asymmetry of bifurcation.

1,2,4,5,6,8-hexafluoronaphthalene Absolute Energy and Cartesian Coordinates (Å)

E = –981.5363710 a.u.

C	2.484744	0.436443	0.000037
C	1.734010	-0.711386	0.000215
C	0.318252	-0.646001	0.000134
C	-0.318252	0.646003	-0.000136
C	0.519809	1.791177	-0.000310
C	1.884281	1.702295	-0.000227
C	-0.519809	-1.791176	0.000308
C	-1.734016	0.711387	-0.000216
H	2.495933	2.594318	-0.000362
C	-2.484746	-0.436441	-0.000039
C	-1.884278	-1.702293	0.000225
H	-2.495931	-2.594315	0.000362
F	-0.036753	3.012651	-0.000561
F	-2.364265	1.892615	-0.000464
F	-3.822273	-0.351438	-0.000117
F	0.036766	-3.012645	0.000562
F	2.364259	-1.892613	0.000467
F	3.822269	0.351424	0.000120

1,2,4,6,8-pentafluoronaphthalene Absolute Energy and Cartesian Coordinates (Å)

E = –882.2879483 a.u.

C	-2.647731	0.230818	0.000077
C	-1.703585	1.217714	0.000255
C	-0.336623	0.848541	0.000168
C	0.052609	-0.532234	-0.000103
C	-0.996284	-1.489524	-0.000277
C	-2.317689	-1.135053	-0.000191
H	-1.991877	2.259035	0.000459
C	0.693312	1.818490	0.000343
C	1.431919	-0.856641	-0.000182
H	-3.089799	-1.892394	-0.000327
C	2.378370	0.137321	-0.000003
C	2.020527	1.494600	0.000263
H	2.786682	2.258047	0.000400
F	-0.688314	-2.795663	-0.000528
F	1.836739	-2.133921	-0.000431
F	3.679911	-0.189112	-0.000083
F	0.331555	3.117581	0.000596
F	-3.954776	0.553460	0.000155

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Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.