Electronic Supplementary Information (ESI)

to the paper entitled

Anion– and lone pair–arene interactions are directional

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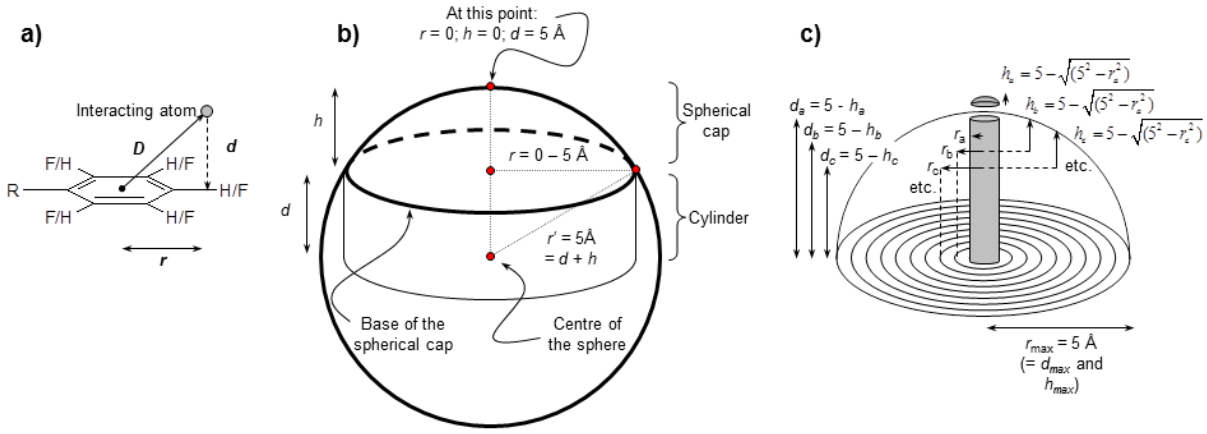
Figure S1. a) Metric parameters obtained from the CSD searches; *r* = radius; *d* = height, and *D* = electron rich atom−ring centroid distance; b) definitions of parameters used to compute the volumes of a spherical cap and a cylinder (with identical radius *r*) that are located within a hemisphere (with radius *r'* = 5 Å); c) illustration showing the spatial indentation (of an hemisphere of r_{max} = 5 Å) applied to analyse the CSD data retrieved (see text for further explanation).



Mathematical procedure to determine the percentage of hits in a certain portion (volume) of a hemisphere (Fig. S1c), i.e. P_n, and the probability P_n* to find hits in this portion of hemispheric volume.

The volume of a hemisphere with a basal radius of 5 Å is equal to half the volume of a sphere with a radius of 5 Å:

(1) $$V_{hemisphere} = \tfrac{1}{2} V_{sphere} = 0.5 \times \tfrac{4}{3} \pi 5^3 = 261.80 Å^3$$

The volume of a cylinder with radius (*r*) and height (*d*) is given by:

(2) $$V_{cylinder} = \pi r^2 d$$

When a cylinder is placed inside a hemisphere so that the top-edges of the cylinder touch the shell of this hemisphere (see S1b), there remains a volume above the cylinder, which is equal to the volume of a spherical cap. The volume of a spherical cap depends on its height (*h*) and basal radius (*r*):

(3) $$V_{spherical\ cap} = \frac{\pi h}{6}(3r^2 + h^2)$$

The height (*h*) of this spherical cap depends partially on the radius (*r*) of the base of the spherical cap. In the present case, this radius is identical to that of the cylinder above which the spherical cap is located (see S1b). The height (*h*) of the spherical cap also depends on the radius (*r'*) of the initial hemisphere. Hence, the height of the spherical cap is given by:

(4) $$h = r' - \sqrt{(r'^2 - r^2)}$$

As the initial hemisphere has a radius of 5 Å, equation

(4) can be rewritten as:

(5) $$h = 5 - \sqrt{(5^2 - r^2)}$$

The height of the spherical cap (*h*) and the height of the cylinder (*d*) are related to each other (see S1b), according to:

(6) $$h + d = 5 Å$$

As a result, equations (2) and (3) can be rewritten as follows:

(7) $$V_{cylinder} = \pi r^2 \left(5 - \left(5 - \sqrt{(5^2 - r^2)}\right)\right)$$

(8) $$V_{spherical\ cap} = \frac{\pi\left(5 - \sqrt{(5^2 - r^2)}\right)}{6}\left(3r^2 + \left(5 - \sqrt{(5^2 - r^2)}\right)^2\right)$$

The total volume of the body inside the hemisphere located above the region with radius (r) is thus given by (see also the grey-coloured volume in Figure S1c):

(9)

$$V(r) = V_{cylinder} + V_{spherical\ cap} = \pi r^2 \left(5 - \left(5 - \sqrt{(5^2 - r^2)}\right)\right) + \frac{\pi\left(5 - \sqrt{(5^2 - r^2)}\right)}{6}\left(3r^2 + \left(5 - \sqrt{(5^2 - r^2)}\right)^2\right)$$

However, the arene rings also occupy a certain volume within the hemisphere, which also depends on r (*vide infra* for the determination of the volume of a C_6H_6 and a C_6F_6 ring as a function of r). Thus, equation (9) can be rewritten as follows:

(10) $$V(r) = V_{cylinder} + V_{spherical\ cap} - V_{arene}$$

Thus, the volume fraction where hits obtained when considering the radius r_r, namely Φ_r, is given by:

(11)

$$\Phi_r = \frac{V(r)}{V_{hemisphere}} = \frac{\pi r^2 \left(5 - \left(5 - \sqrt{(5^2 - r^2)}\right)\right) + \frac{\pi\left(5 - \sqrt{(5^2 - r^2)}\right)}{6}\left(3r^2 + \left(5 - \sqrt{(5^2 - r^2)}\right)^2\right) - V_{arene}(r)}{0.5 \times \frac{4}{3}\pi 5^3}$$

Similarly, the volume fraction where hits obtained when considering an inner radius r_a and an outer radius r_b (see Fig. 3), namely $\Phi_{b\text{-}q}$, is given by:

(12) $$\Phi_{b-a} = \frac{\left(V_{cylinder}(r_b) + V_{spherical\ cap}(r_b) - V_{arene}(r_b)\right) - \left(V_{cylinder}(r_a) + V_{spherical\ cap}(r_a) - V_{arene}(r_a)\right)}{V_{hemisphere}}$$

which can be written mathematically as:

(13)

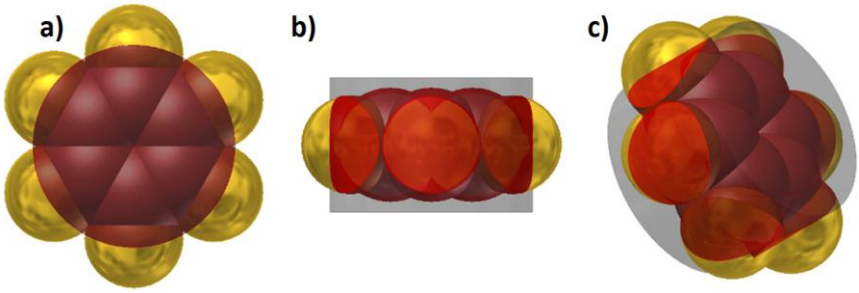
$$\Phi_{b-a} = \frac{\left(\pi r_b^2 \left(5 - \left(5 - \sqrt{(5^2 - r_b^2)}\right)\right) + \frac{\pi\left(5 - \sqrt{(5^2 - r_b^2)}\right)}{6}\left(3r_b^2 + \left(5 - \sqrt{(5^2 - r_b^2)}\right)^2\right) - V_{arene}(r_b)\right) - \left(\pi r_a^2 \left(5 - \left(5 - \sqrt{(5^2 - r_a^2)}\right)\right) + \frac{\pi\left(5 - \sqrt{(5^2 - r_a^2)}\right)}{6}\left(3r_a^2 + \left(5 - \sqrt{(5^2 - r_a^2)}\right)^2\right) - V_{arene}(r_a)\right)}{0.5 \times \frac{4}{3}\pi 5^3}$$

In this study, Φ_r were computed with r increments of 0.05 Å, thus producing a total of 100 data-points for a hemisphere of r = 5 Å.

Procedure to determine a portion of the volume of C_6H_6 and C_6F_6 as a function of *r*.

The C_6H_6 and C_6F_6 molecules were drawn as parts (.ipt extension) using the 3D drawing program Autodesk® Inventor® (Version 2012), using bond distances of 1.40 (C – C), 1.09 (C – H), and 1.35 (C – F) Å, and considering van der Waals radii of 1.70 (C), 1.09 (H), and 1.47 (F) Å. Next, several cylinders were drawn (also as parts (.ipt extension)) with a height of 4 Å and with radii (*r*) ranging between 0 and 5 Å (thus with 0.05 Å increments). The two arene rings and the 100 cylinders were then collected in one assembly file (.iam extension), and the centre of gravity of the arene rings and those of the 100 cylinders were aligned to one another. By using the 'Analyse Interference' option of Autodesk® Inventor®, the shared volume of one of the arenes and a specific cylinder could be computed (See Figure S2 for an illustration of a C_6F_6 / Cylinder (r = 3.0 Å)). This was repeated for all 100 cylinders, giving the volume of an arene as a function or *r*. Obviously, this volume is equal to the volume of the entire arene at *r*-values larger than that of the 'edge' of the arene (i.e., 3.58 Å for C_6H_6 and 4.22 Å for C_6F_6) Å).

Figure S2. Illustration of the method used to compute the overlapping volume (in red) between an arene (C_6F_6 in this case) and a cylinder (grey), with r = 3 Å and height = 4 Å. a) top view; b) side view; c) perspective view.



Data extraction form the CSD

The datasets including the *inter*molecular interactions investigated were obtained from the Cambridge Structural Database (CSD) version 5.32 (November 2010 including one update).[1] A cut-off distance (*D*) of 5 Å between the interacting atom and the centre of the arene ring (ring centroid) was applied using the ConQuest program (version 1.12, 2010).[2] The crystallographic discrepancy factor was always set on the same value ($R_f \leq 0.10$), and all powder structures and structures that contained errors were excluded using the ConQuest search filter. Disordered structures were taken into account because anion– or lone-pair–π interactions may cause disorder.

First, two datasets were generated that contained respectively all $–C_6H_5$ and all $–C_6F_5$ rings found in the CSD. From these datasets, two subsets were created that contained both the arene and an electron-rich atom (i.e., any halogen (Hlg.), N, P, As, O, S, Se, and Te)). From these two subsets, the *D* and *d* values (see Figure S1a) were extracted for all hits for which the interacting atom was at a distance below or equal to 5 Å from the centre of the ring (*inter*molecular interaction). The numbers of CIFs obtained together with the corresponding hits for these six CSD searches are listed in Table S1.

Table S1. Number of hits observed in the CIFs collected to generate the two subsets corresponding to the electron-rich atom (molecule)···arene pairs investigated in the present study.

Arene ↓	hits	CIFs
$–C_6H_5$	727,491	101,549
$–C_6F_5$	50,086	3,945

[1] F. H. Allen, *Acta Cryst.* **2002**, *B58*, 380.

[2] ConQuest - The Interface for the CSD System; http://www.ccdc.cam.ac.uk/products/csd_system/conquest/

Distribution of hits (P_n) and determination of the probability value (P_n^*) to find a hit within a defined very small portion of the hemisphere considered for the CSD study

For the CSD searches herein reported, a cut-off distance *D* (see Figure S1a) of 5 Å was applied, and the distances between the different interacting atoms and the plane of the two aryl rings (*d*) were extracted. The parallel displacement parameter (*r*) for each hit can be obtained using Pythagoras' theorem:

$$r = \sqrt{D^2 - d^2} \quad (14)$$

This parallel displacement parameter is mathematically equivalent to the radius of a sphere whose centre corresponds to the centre of the plane of the aromatic ring. Thus, the data retrieved from the CSD were divided in datasets based on *r* increments of 0.05 Å. The amount of hits (N_n) found within a specific small portion of the hemispheric volume (for example between r_a and r_b; n = b−a → N_{b-a}) relative to the total amount of hits within the 5 Å hemispheric pocket (N_{tot}) characterises the percentage (P_n) of hits found in the volume defined by r_n. For instance, for the volume defined by $r_b - r_a$ (see Figure 3, centre), the corresponding percentage P_{b-a} is given by:

$$P_{b-a} = \frac{N_{b-a}}{N_{tot}} \quad (15)$$

The probability value P_n^* (see below) to find a hit within a volume defined by r_n should then be unity if the distribution of the hits above the arene ring is random.

$$P^*_{b-a} = \frac{P_{b-a}}{\Phi_{b-a}} \quad (16)$$

Accordingly, any significant deviation of P_n^* from unity is indicative of a non-accidental distribution of the corresponding interacting atom over the aromatic ring. Hence, $P_n^* < 1$ reflects unfavourable atom···arene interactions, while the opposite situation is characterised by $P_n^* > 1$ (see P_n^* *vs*. *r* plots in the main text).