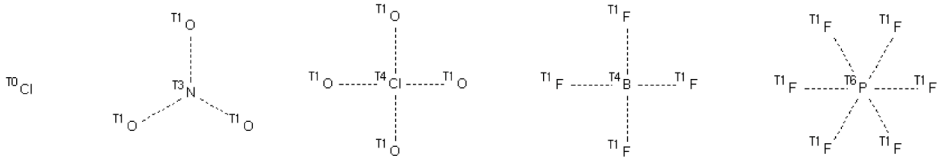
CSD search specifications

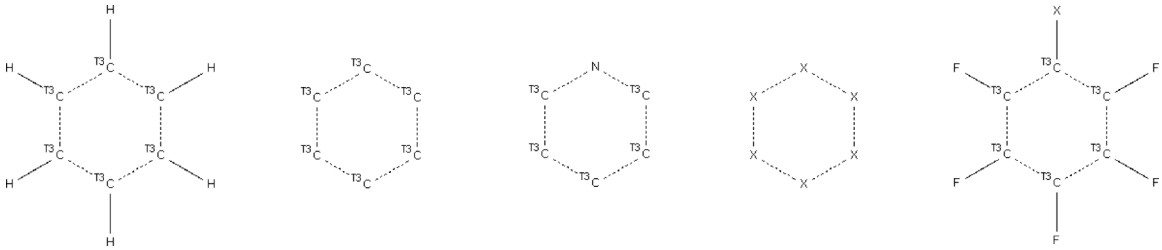
Searches were performed using ConQuest version 1.10 with the CSD Database version 5.29 (November 2007). The following filters were applied to every search: 3D coordinates determined, $r_{fac} \leq 0.10$, not disordered, and no errors.

Definition of anions – All anion structures were specified in such a way as to exclude any species that were coordinated to metal ions, alkylated, or protonated. This was done by specifying the number of bonded atoms for each atom in the anion. To avoid possible problems with bond order specifications, all bonds in polyatomic anions were specified as 'any' bond. The anions look like this on the ConQuest draw screen:



Definition of other contacting groups – To search for contacts between aliphatic methyl group hydrogen atoms and C_6H_6, we defined a molecule $R_3C\text{-}CH_3$, where R is any carbon or hydrogen atom. To search for contacts between potassium and any planar C_6 ring, we used a potassium atom. To search for contacts between any heteroatom and any planar C_6F_5X ring, we defined an element group containing N, O, S, F, Cl, and Br and then used an atom of this element.

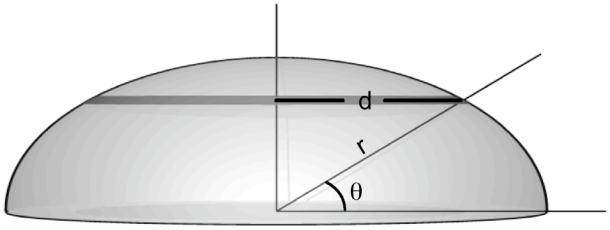
Definition of arenes – Five six-membered ring structures were specified. These include C_6H_6 (benzene), any planar C_6 arene, any planar C_5N arene, X_6 (any six-membered ring), and C_6F_5X (any planar perfluoronated arene). To avoid possible problems with bond order specifications, all ring bonds were specified as 'any' bond. Planar rings were selected by specifying three bonded atoms to each carbon in C_6H_6, C_6, C_5N, and C_6F_5X. In the case of X_6, all possible rings were included in the search and the few nonplanar rings that were obtained were removed by visual inspection. The rings look like this on the ConQuest draw screen:



Data for distribution plots and histograms – Initial large data sets for the distribution of species around six-membered rings were collected by searching for nonbonded intermolecular contacts between the ring centroid and an atom of the contacting species. All data within a 0.0 to 7.0 Å range were retained (contacting species, contacting atom): R_3CH_3, H; chloride, Cl; nitrate, N; perchlorate, Cl; tetrafluroborate, B; hexafluorophosphate, P; any heteroatom, N, O, S, F, Cl, or Br. Geometric parameters from each search were exported to a spreadsheet file. Plots of d_{offset} versus d_{plane} (see manuscript) revealed that in each case the data were distributed over a void that had the approximate shape of an oblate ellipsoid. The original dataset was trimmed to retain only those points within 1.0 Å of the inner elliptical perimeter, yielding the subsets of data shown in the manuscript figures.

Structures that resemble calculated anion-π geometries – 3D searches for anions that were in nonbonded contact with six-membered rings and look like geometries expected for anion-π complexes were performed using the following constraints. First, the anion should be roughly centered over the ring. This requirement was imposed by restricting the angle between the ring plane and the vector from the anion center to the ring centroid to be 0 ± 10° (corresponding to a tilt angle $\theta = 90 \pm 10°$ as described in the manuscript). Second, the anion should be close to the arene surface. For halides, nonbonded contacts between the anion and each of the six ring atoms had to be ≤ Σvdw radii + 0.2 Å. For polyatomic anions, and three of the anion atoms, O or F, had to be in contact with three ring atoms (with either a 1,3,5 or a 2,4,6 pattern) such that all three contact distances were within Σvdw radii + 0.2 Å.

Probability of being at a tilt angle θ on the surface of an oblate ellipsoid



Probability to be at any arbitrary position on the surface of the ellipsoid can be expressed in terms of the tilt angle, θ. It is given by the ratio of the surface area of the sector at angle θ (dark grey) to the total surface area.

sector area = circumference • width

$$= 2\pi \int_{\theta_1}^{\theta_2} d \bullet r \, d\theta$$

$$= 2\pi \int_{\theta_1}^{\theta_2} r \sin\theta \bullet r \, d\theta$$

$$= 2\pi \int_{\theta_1}^{\theta_2} r^2 \sin\theta \, d\theta$$

$$= 2\pi a^2 \int_{\theta_1}^{\theta_2} \frac{\sin\theta \, d\theta}{1 + c \sin^2\theta}$$

$$= 2\pi a^2 \left\{ 1/2 \left(\frac{a^2 - b^2}{b^2} \right) \theta \; - 1/4 \left(\frac{a^2 - b^2}{b^2} \right) \sin(2\theta) \; - \cos\theta \right\} \Bigg|_{\theta_1}^{\theta_2}$$

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1; \text{ equation of ellipse}$$

$$x = r\cos\theta; \; y = r\sin\theta$$

$$\frac{r^2\cos^2\theta}{a^2} + \frac{r^2\sin^2\theta}{b^2} = 1$$

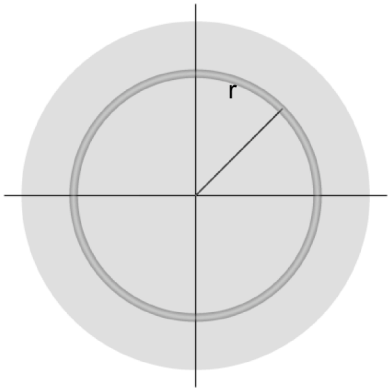
$$r = \frac{ab}{(b^2\cos^2\theta + a^2\sin^2\theta)^{1/2}}$$

$$\cos^2\theta = 1 - \sin^2\theta; \text{ identity}$$

$$r = \frac{a}{(1 + c\sin^2\theta)^{1/2}}; \; c = \frac{a^2 - b^2}{b^2}$$

Using this equation, sector areas were evaluated from θ = 0 to 90° in 2° intervals for an oblate ellipsoid approximately the shape of a benzene molecule (a = 1.5 Å and b = 1.0 Å). Summing these sector areas yields the total area. Dividing each sector area by the total area gave the probability to exhibit a given θ value. Histograms for random distributions of tilt angles that are compared with the experimental distributions in the paper were generated by multiplying the total number of experimental data points by these probabilities.

Probability of being at a radial distance from the center of a circle



Probability to be at any distance from the center of a circle can be expressed in terms of the radius, r. It is given by the ratio of the surface area of the sector at distance r (dark grey) to the total surface area of the circle.

sector area = $\pi(r+\Delta r)^2 - \pi r^2$; where Δr = sector width

$= \pi(r^2+2r\Delta r+\Delta r^2) - \pi r^2$

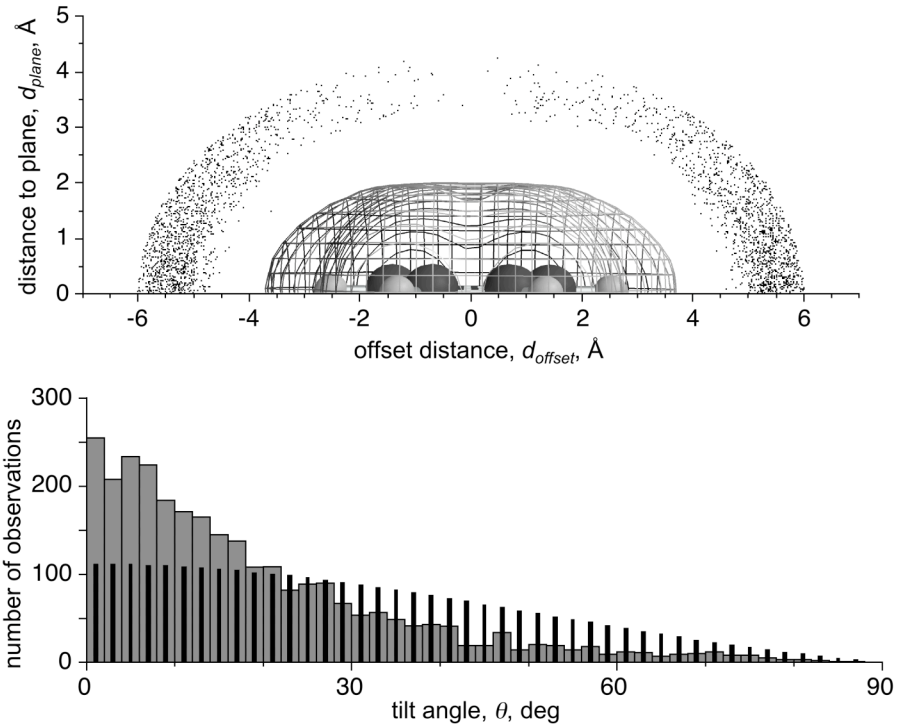
$= \pi(2r\Delta r+\Delta r^2))$

if Δr is constant, then . . .

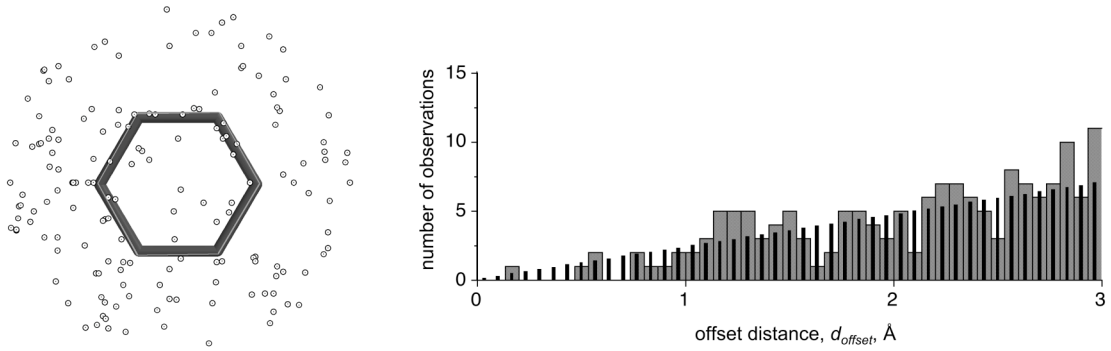
= a r + b; where a and b are constants

Thus, we see that the probability to be at any distance from the center of the circle is a linear function of the distance. Normalized probabilities were computed from r = 0 to 3 Å in 0.0666 Å increments, yielding 45 bins. Histograms for random distributions of d_{offset} values that are compared with the experimental distributions in the paper were generated by multiplying the total number of experimental data points by these probabilities.

Distributions for NO_3^- contacting any flat C_6 ring

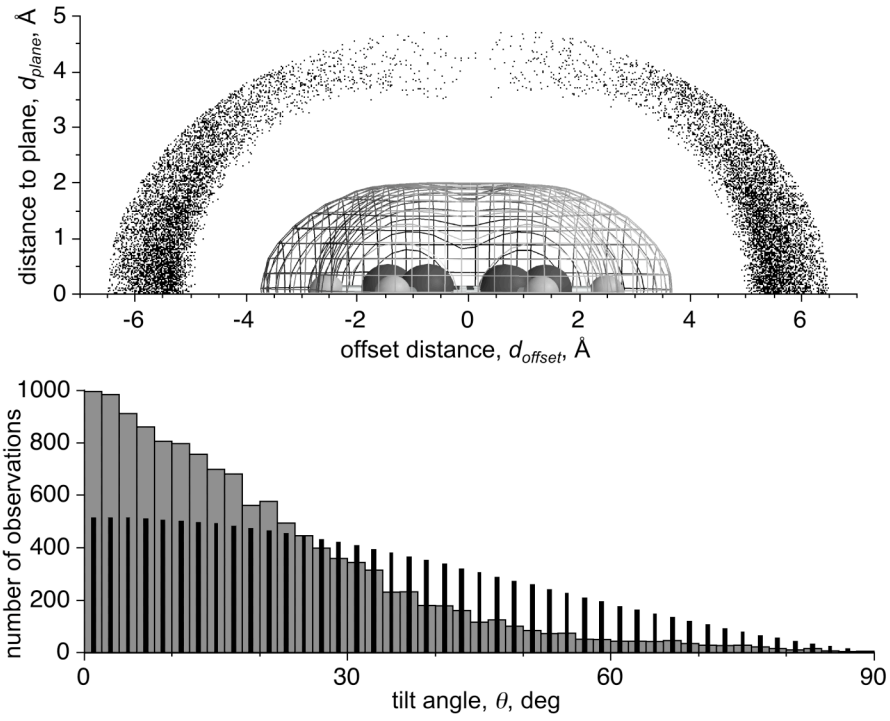


Distribution of contacts between nitrate and C_6 in the CSD. The upper plot shows the position of 2813 nitrate nitrogen atoms within ± 1 Å of an oblate ellipsoid (a=b=5.0, c=3.3 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

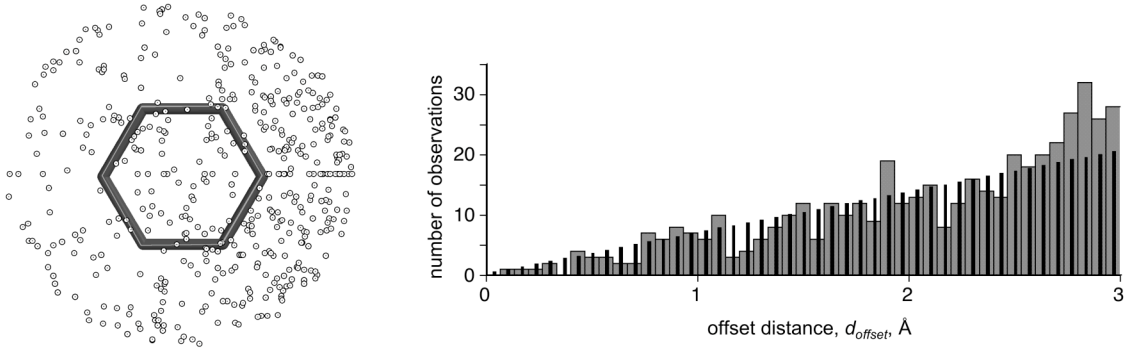


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 161 nitrate nitrogen atoms 2.72 to 3.72 Å above the C_6 plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for ClO_4^- contacting any flat C_6 ring

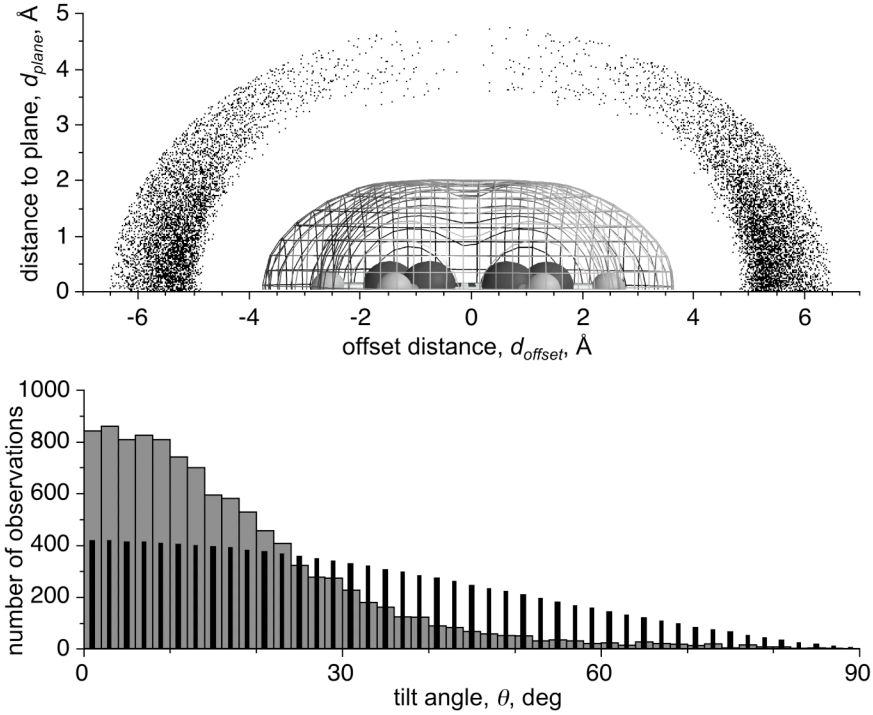


Distribution of contacts between perchlorate and C_6 in the CSD. The upper plot shows the position of 13.023 perchlorate chlorine atoms within ± 1 Å of an oblate ellipsoid (a=b=5.5, c=3.8 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

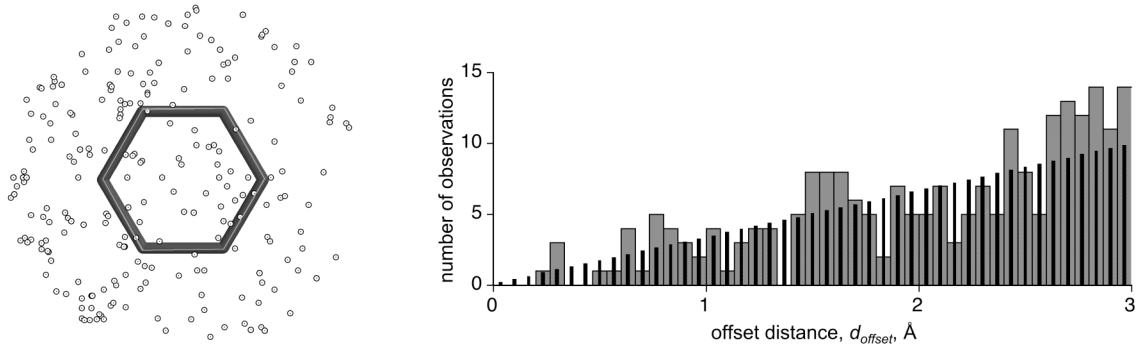


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 470 perchlorate chlorine atoms 3.2 to 4.2 Å above the C_6 plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for BF_4^- contacting any flat C_6 ring

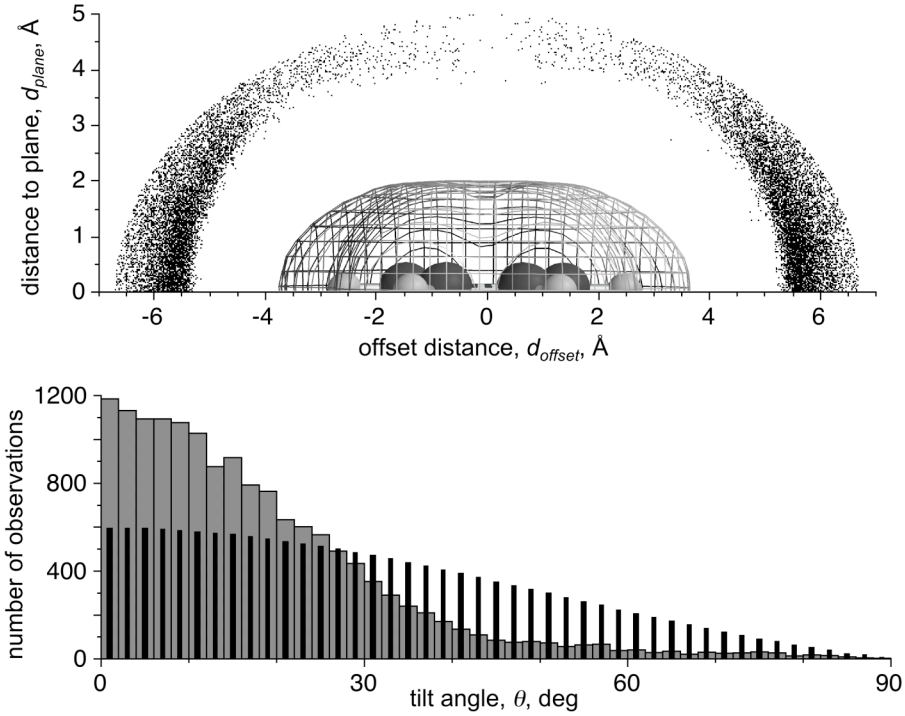


Distribution of contacts between tetrafluoroborate and C_6 in the CSD. The upper plot shows the position of 10,562 tetrafluoroborate boron atoms within ± 1 Å of an oblate ellipsoid (a=b=5.5, c=3.8 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

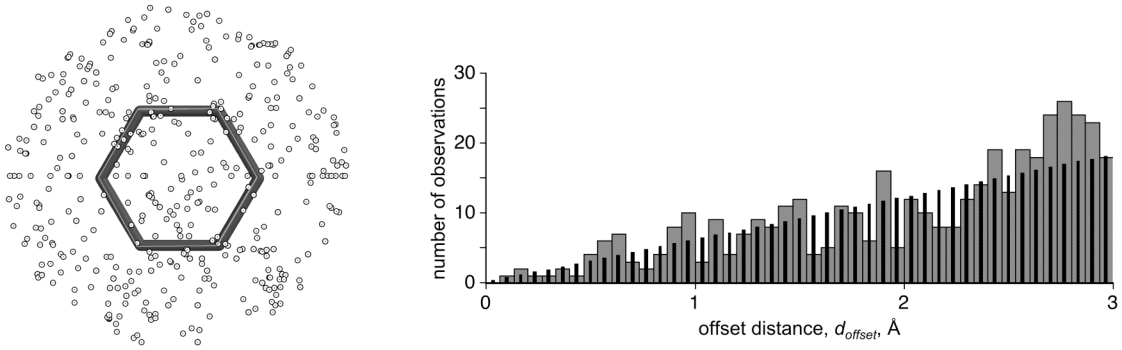


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 227 tetrafluoroborate boron atoms 3.14 to 4.14 Å above the C_6 plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for PF_6^- contacting any flat C_6 ring

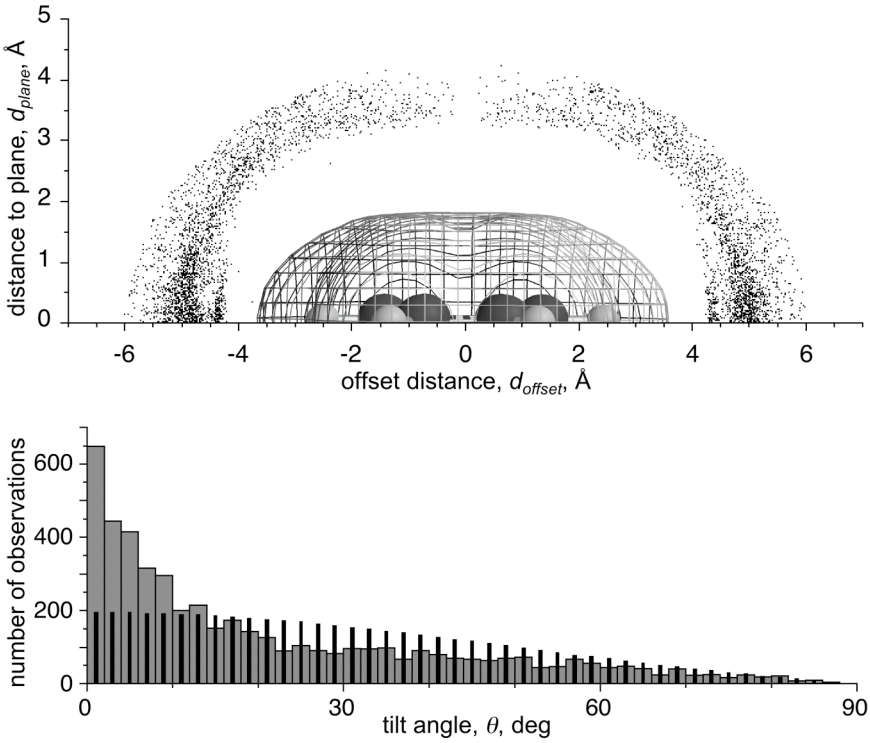


Distribution of contacts between hexafluorophosphate and C_6 in the CSD. The upper plot shows the position of 15,046 hexafluorophosphate phosphorous atoms within ± 1 Å of an oblate ellipsoid (a=b=5.7, c=4.0 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

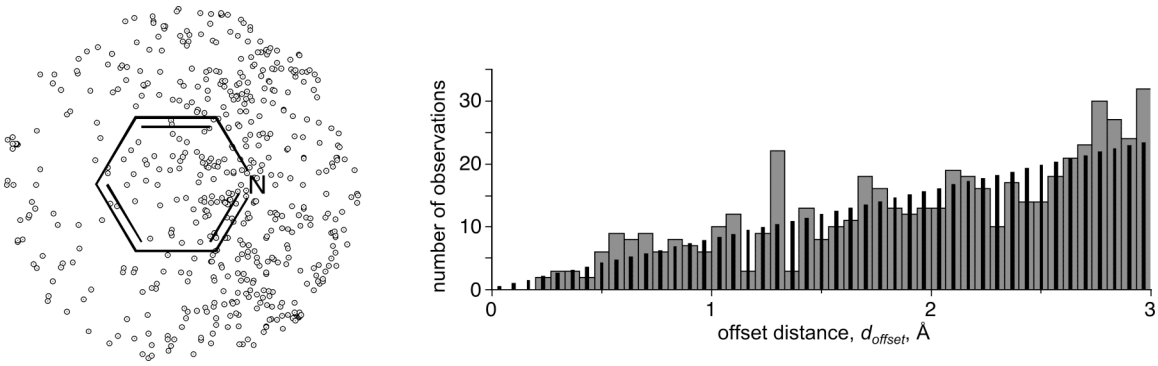


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 420 hexafluorophosphate phosphorous atoms 3.58 to 4.58 Å above the C_6 plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for Cl^- contacting any flat C_5N ring

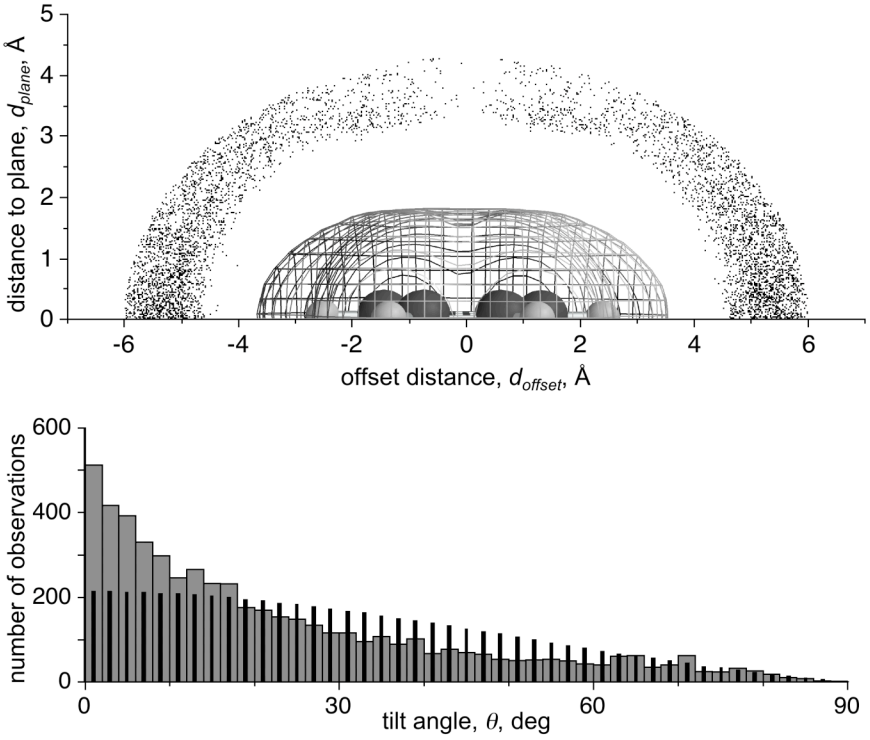


Distribution of contacts between chloride anions and C_5N in the CSD. The upper plot shows the position of 4,930 chloride anions within ± 1 Å of an oblate ellipsoid (a=b=5.0, c=3.3 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

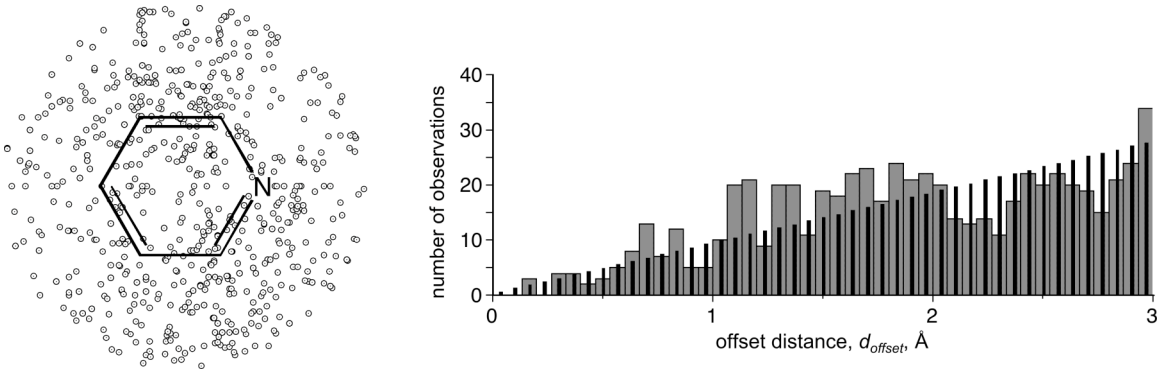


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 538 chloride anions 2.66 to 3.66 Å above the C_5N plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for NO_3^- contacting any flat C_5N ring

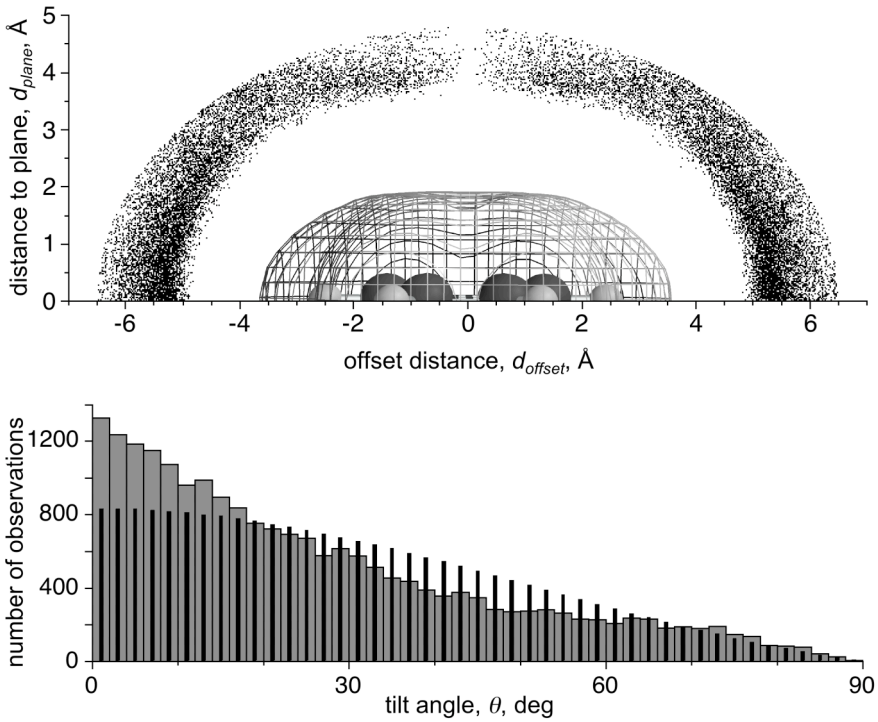


Distribution of contacts between nitrate anions and C_5N in the CSD. The upper plot shows the position of 5,383 nitrate nitrogen atoms within ± 1 Å of an oblate ellipsoid (a=b=5.0, c=3.3 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

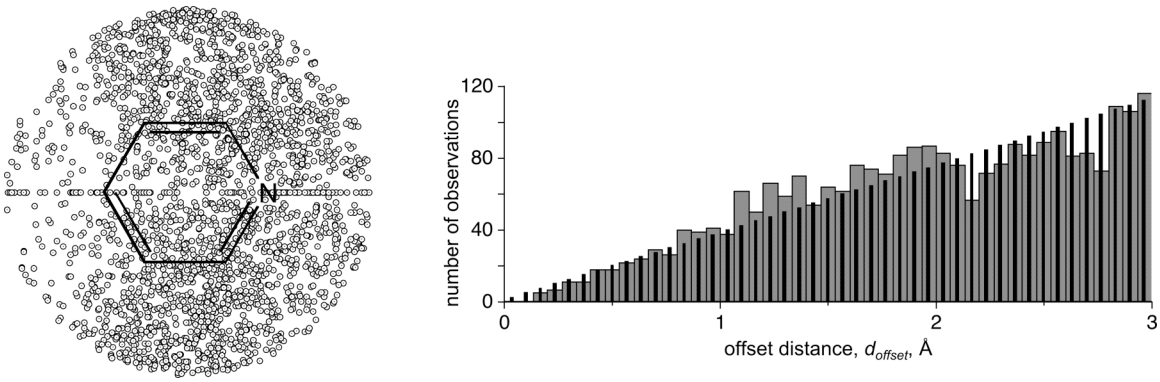


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 635 nitrate nitrogen atoms 2.72 to 3.72 Å above the C_5N plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for ClO_4^- contacting any flat C_5N ring

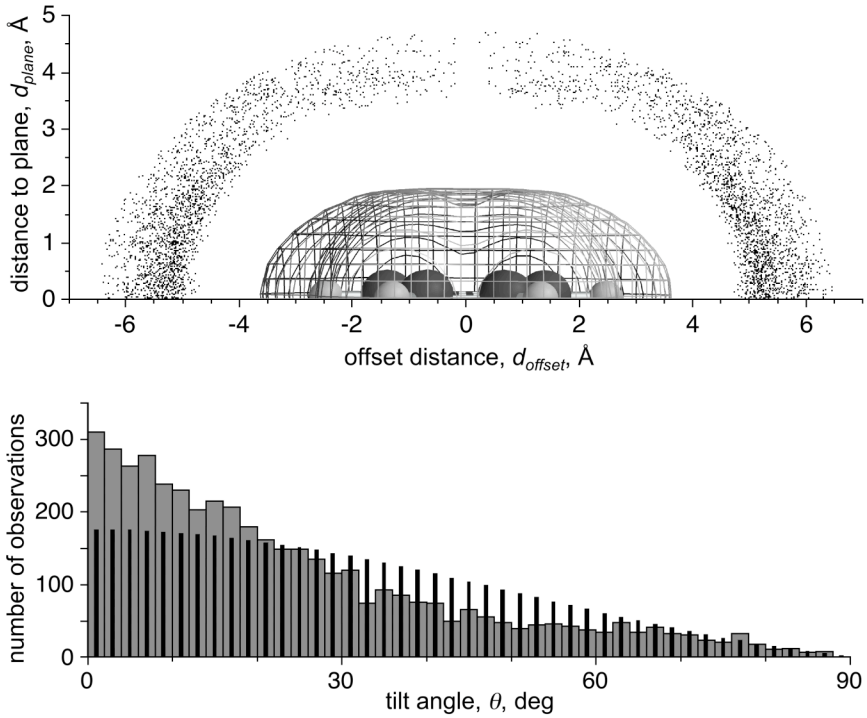


Distribution of contacts between perchlorate anions and C_5N in the CSD. The upper plot shows the position of 21,006 perchlorate chloride atoms within ± 1 Å of an oblate ellipsoid (a=b=5.5, c=3.8 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

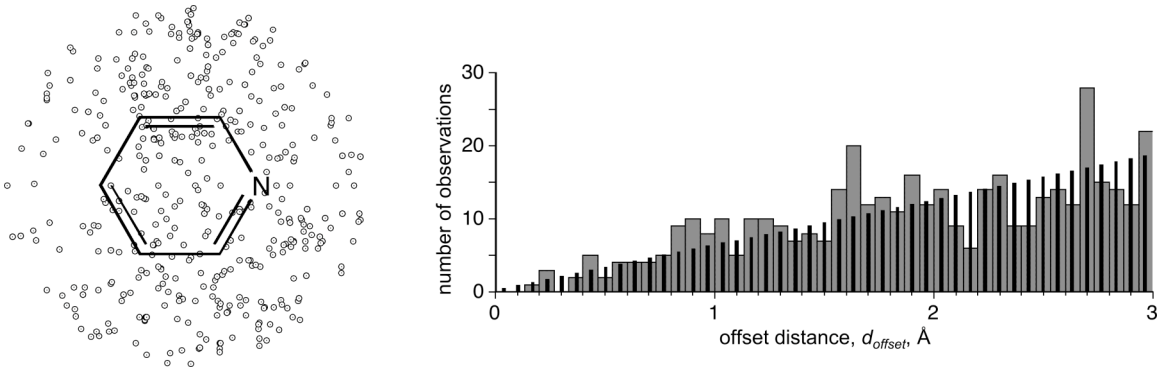


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 2579 perchlorate chloride atoms 3.20 to 4.20 Å above the C_5N plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for BF_4^- contacting any flat C_5N ring

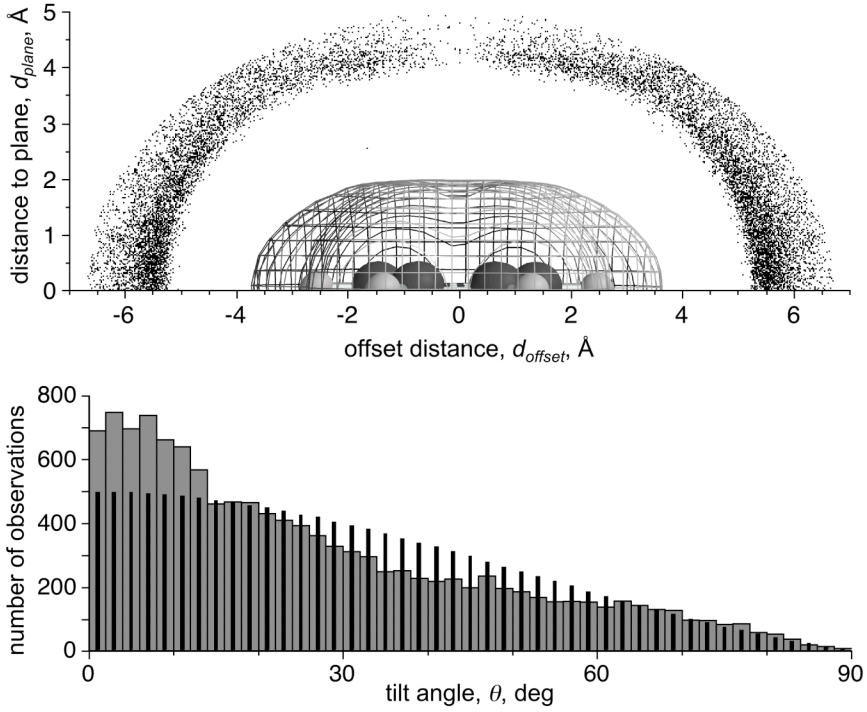


Distribution of contacts between tetraflouroborate anions and C_5N in the CSD. The upper plot shows the position of 4,436 tetrafluoroborate boron atoms within ± 1 Å of an oblate ellipsoid (a=b=5.5, c=3.8 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.

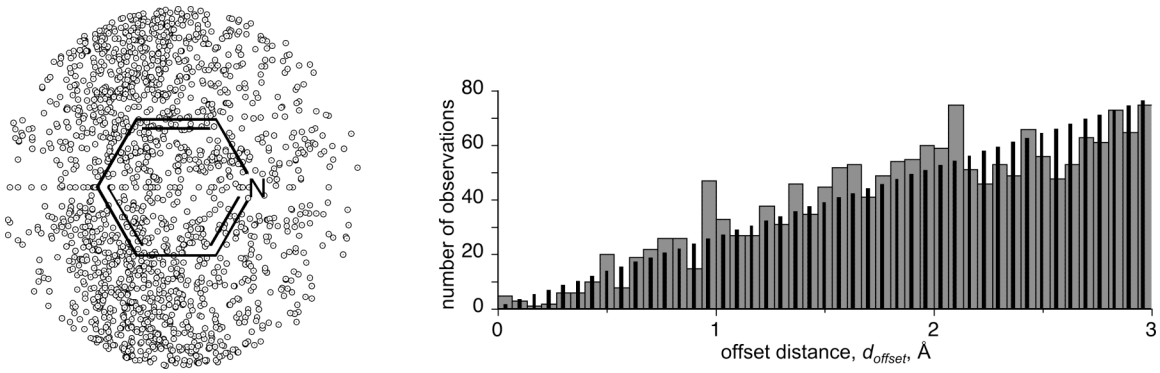


Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 428 tetrafluoroborate boron atoms 3.14 to 4.14 Å above the C_5N plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.

Distributions for PF_6^- contacting any flat C_5N ring



Distribution of contacts between hexaflourophosphate anions and C_5N in the CSD. The upper plot shows the position of 12,574 hexaflourophosphate phosphorous atoms within ± 1 Å of an oblate ellipsoid (a=b=5.7, c=4.0 Å). The lower plot shows the comparison of experimental versus random (thin black bars) tilt angle, θ, distributions.



Looking down from above with $d_{offset} \leq 3$ Å, the left plot shows the location of 1755 hexaflourophosphate phosphorous atoms 3.58 to 4.58 Å above the C_5N plane. The right plot shows the comparison of experimental versus random (thin black bars) d_{offset} distributions.