Supplementary material for

From attraction to repulsion: Anion-π interactions between bromide and fluorinated phenyl groups

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Single crystal X-ray analysis

The structure **2a** is already described in the literature by us.[S1] The crystallographic information file (CIF) can be obtained from Cambridge Structural Database (webcsd.ccdc.cam.ac.uk) or free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif) with reference code/number TUTKAV or CCDC-752834.

The crystals suitable for single crystal X-ray diffraction analyses were obtained from CH_3CN (**2a**), MeOH/EtOAc (**2b**), DMF/EtOAc (**2c**, **2g**) or DMF/Et_2O (**2d**-**2f**) solutions. The structural data were collected at 123.0 ± 1 K with Bruker-Nonius KappaCCD diffractometer equipped with APEXII detector, using graphite monochromatized MoK_α radiation (λ = 0.71073 Å). COLLECT[S2] software was used for data collection and data were processed with DENZO-SMN.[S3] The structures were solved by direct methods, using SIR-2004[S4] and refined on F^2, using SHELXL-97.[S5] The multi-scan absorption correction (SADABS[S6]) was enabled to all data. The H atoms bonded to C atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C atom temperature factor) and refined as riding atoms. The H atoms bonded to O atoms in were found from electron density map and fixed to distances of 0.84 Å from O atom (DFIX) with isotropic temperature factor (1.5 times the O atom temperature factor). The figures for the article were drawn with ORTEP-3[S7], MERCURY[S8] and POV-RAY[S9]. The figures for Supplementary material were drawn with ORTEP-3[S7]. The crystallographic information file (CIF) of **2b-g** can be obtained from Cambridge Structural Database (webcsd.ccdc.cam.ac.uk) or free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif) with reference numbers CCDC 817432 - 817437

The following representations show the closest contacts of the bromide anions of compounds **2a-e** which are present in addition to anion-π interactions. CH-bromide separations below 3.00 Å are shown by dashed lines.

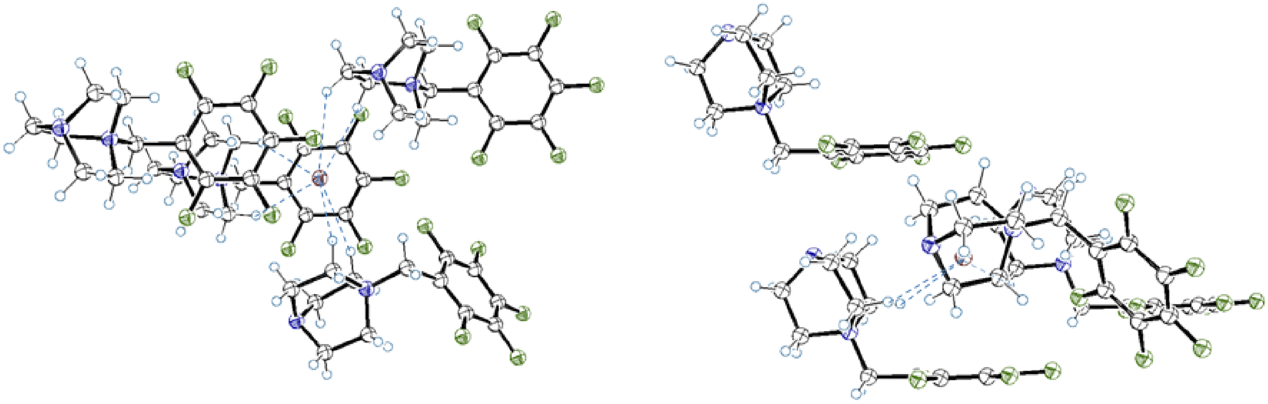


Figure S1. Two different views of all contacts of bromide found in compound **2a**.

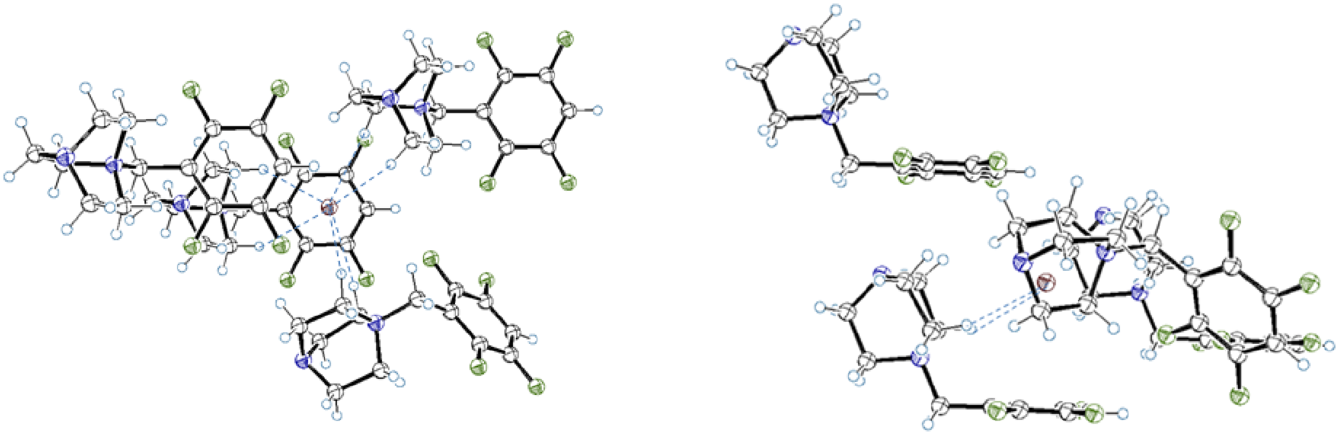


Figure S2. Two different views of all contacts of bromide found in compound **2b**.

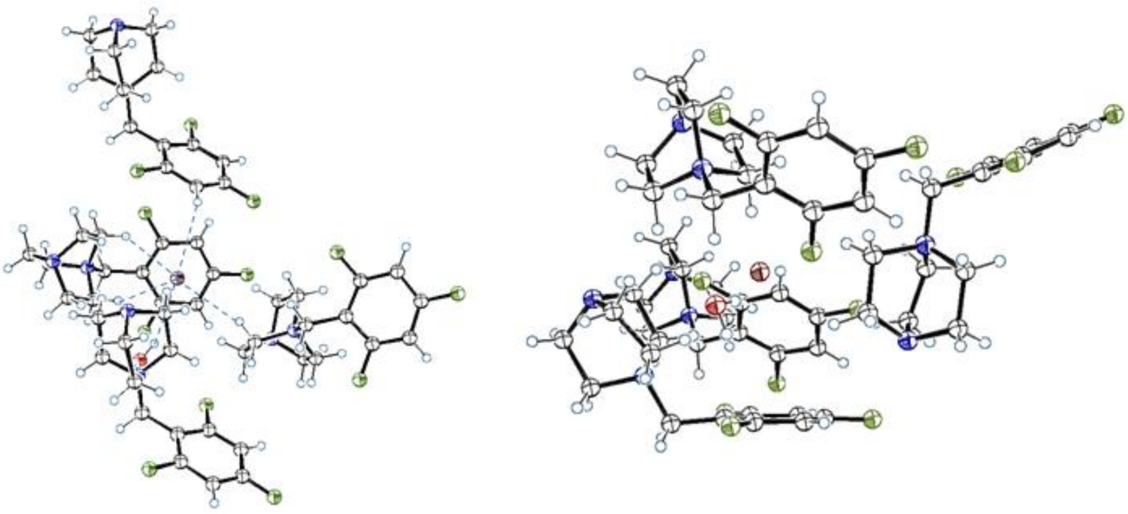


Figure S3. Two different views of all contacts (CH as well as OH_{water} anion hydrogen bonding) of bromide found in compound **2c**.

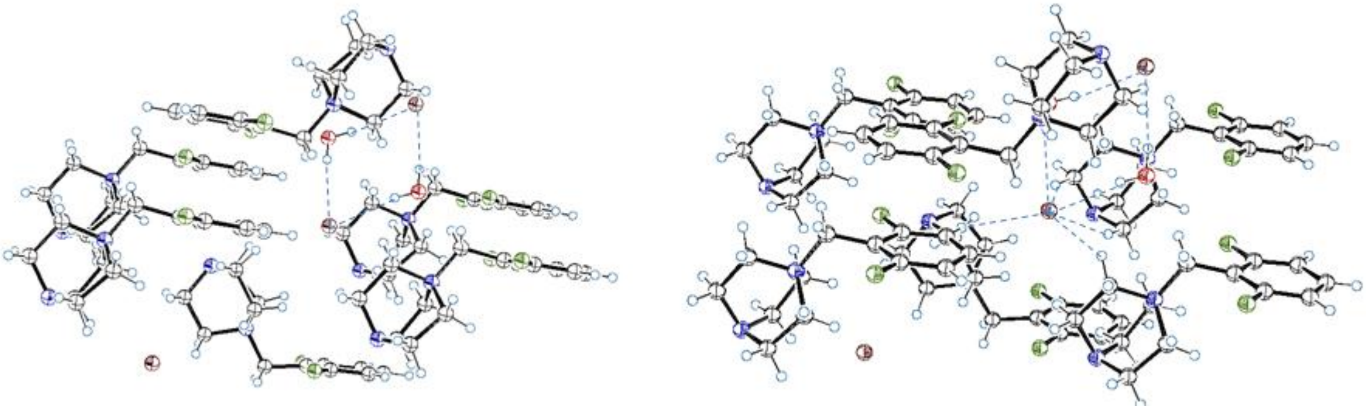


Figure S4. Two different views of all contacts (CH as well as OH_{water} anion hydrogen bonding) of bromide found in compound **2d**.

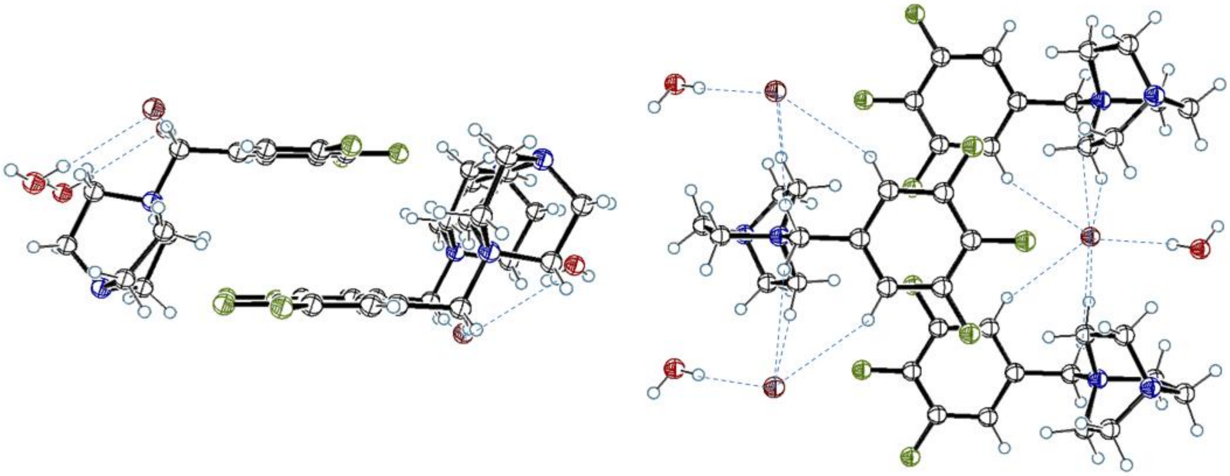


Figure S5. Two different views of all contacts (CH as well as OH_{water} anion hydrogen bonding) of bromide found in compound **2e**.

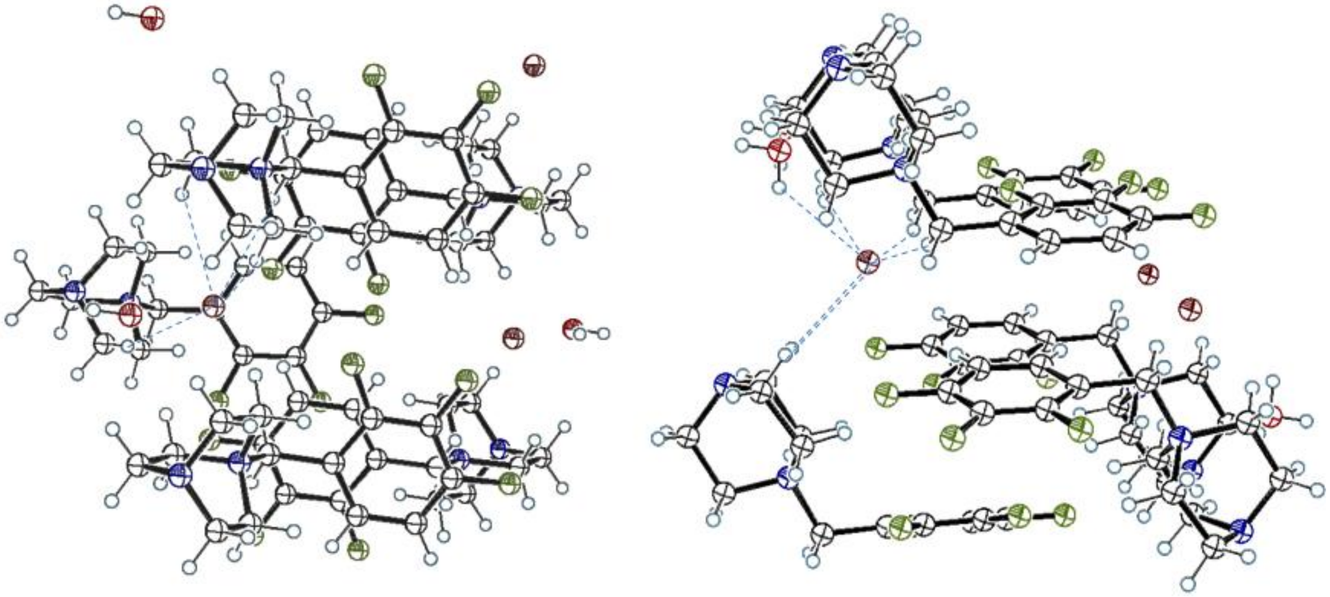


Figure S6. Two different views of all contacts (CH as well as OH_{water} anion hydrogen bonding) of bromide found in compound **2f**.

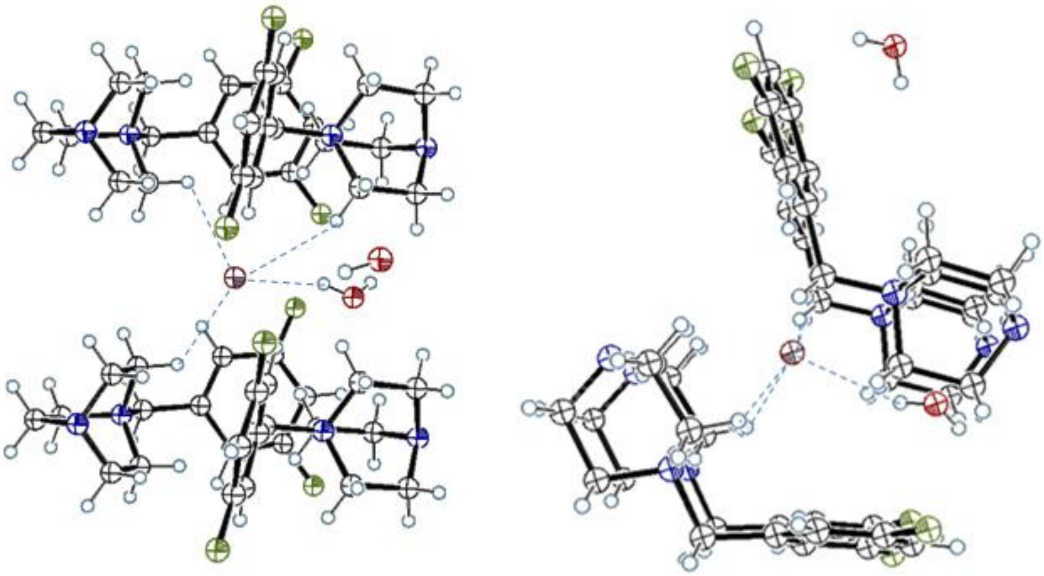


Figure S7. Two different views of all contacts (CH as well as OH_{water} anion hydrogen bonding) of bromide found in compound **2g**.

Computational studies

All *ab initio* calculations were performed using the Gaussian 09[S10] suite of quantum-chemical routines. Starting geometries were generated employing Gaussview 5.0[S11] and the resulting coordinates were then energetically optimized at the MP2/6-311++G** level to locate stationary points. The resulting stationary points were characterized as either local minima or saddle points by normal coordinate analyses which, in addition, provided the corresponding zero-point energies. In the starting geometries for the complexes, the anion was placed above the aromatic ring. The centroid of each of the aromatic systems in the optimized structures was defined as the average value of the coordinates of the centers of those three straight lines that connect two carbon atoms opposite to each other.

The energies of the π-systems without the anions were obtained in the same way as described above. In order to get the bond energy of a system, the sum of the total energies of the aromatic and the anion was subtracted from the total energy of the corresponding salts, where zero-point energies were included for all polyatomic species.

In case of **1e**, an additional geometry optimization was performed starting from a set of coordinates with the anion being located "behind" the substituent. The obtained bond energy for this structure is lower (-99,003 kcal/mol) than the one of the local minimum with the anion above the aromatic ring (-92,323 kcal/mol). Thus, the preferred position of the anion should be that in structure.

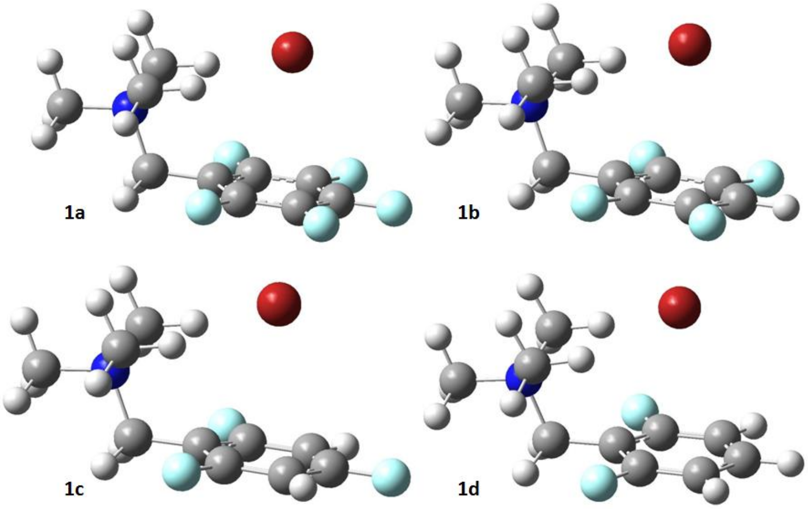
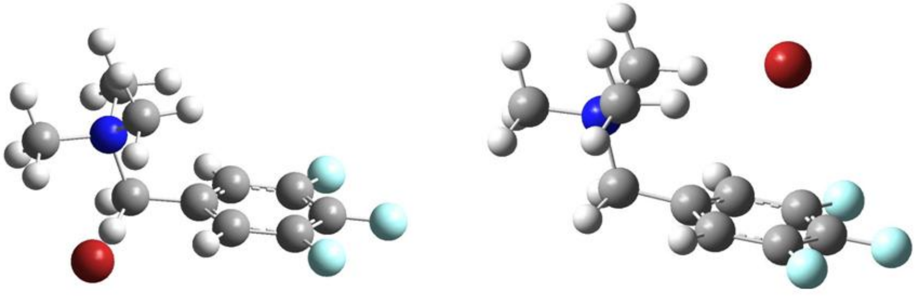


Figure S8. Minimum structure of salts **1a-1d** as found by computation.



1e „side on"
(E = -3313,894645 a.u.)

1e „π-complex"
(E = -3313,883645 a.u.)

Figure S9. Comparison of the favored side on structure and the π-complex of **1e** as found by computation.

Table S1. Total energy, "bond" energy and distance between anion and centroid of the fluorinated aromatic ring [Å].

	energy	bond energy	d(Br-centr)
1a	-3512,025	-96,633	3,274
1b	-3412,962	-93,865	3,320
1c	-3313,900	-91,420	3,362
1d	-3214,824	-88,895	3,415

References

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