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Anion–π Interactions in Salts with Polyhalide Anions: Trapping of I_4^{2-}

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Dedicated to Professor Kazuhisa Hiratani on the occasion of his 65th birthday

Abstract: The directionality of interaction of electron-deficient π systems with spherical anions (e.g,. halides) can be controlled by secondary effects like NH or CH hydrogen bonding. In this study a series of pentafluorophenyl-substituted salts with polyhalide anions is investigated. The compounds are obtained by aerobic oxidation of the corresponding halide upon crystallization. Solid-state structures reveal that in bromide **2**, directing NH–anion interactions position the bromide ion in an η^1-type fashion over but not in the center of the aromatic ring. The same directing forces are effective in corresponding tribromide salt **3**. In the crystal, the bromide ion is paneled by four electron-deficient aromatic ring systems. In addition, compounds **4** and **6**, which have triiodide and the rare tetraiodide dianion as anions, are described. Computational studies reveal that the latter is highly unstable. In the present case it is stabilized by the crystal lattice, for example, by interaction with electron-deficient π systems.

Keywords: computational chemistry · halogens · polyhalides · pi interactions · supramolecular chemistry

Introduction

Supramolecular chemistry is defined as the chemistry of noncovalent interactions. The most prominent of such weak interactions are hydrogen bonding, electrostatic attraction, and metal coordination.[1] Aromatic units can be involved in π–π stacking or cation–π interactions. Recently, an additional type of weak interaction was reported, that is, the anion–π interaction between electron-deficient aromatic rings and anions. Theoretical investigations show that anion–π interactions are attractive.[2,3] Experimental evidence is mainly found in the crystal, but some observations indicate the relevance of this interaction in solution.[4] A large number of experimental examples involve organometallic coordination assemblies, whereas anion–π interactions in purely organic compounds are only rarely described.[5]

Recently, we started systematic studies on anion–π interactions of halide anions in pentafluorophenyl ammonium and phosphonium salts.[6] Crystal structures show high structural versatility in the relative position of the anion to the pentafluorophenyl moieties of the cations. The position of the anion with respect to the π system can be best described by the hapticity (η) nomenclature that was introduced for the extensively investigated cation–π systems.[7] Because of the weak nature of the anion–π interaction a strong directing influence by the substituents of the ammonium and phosphonium cations (mainly NH··· or CH···anion interactions) on the location of the anion was observed.[8] Thus, the interaction between a spherical anion (halide) and an electron-deficient aromatic ring is controlled by 1) the electrostatic interaction between the anion and the aromatic unit, and 2) by the substituents at the periphery of the aromatic ring. With spherical anions, it is mainly the size and the polarizability of the anion that are important. Therefore, it is of interest to investigate derivatives that contain electron-deficient aromatic moieties in addition to linear anionic species (e.g., polyhalide anions).

By serendipity we obtained a series of crystal structures involving linear polyhalide anions (tribromide anion, triiodide anion, and the rare tetraiodide dianion) in crystal latti-

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ces containing electron-deficient pentafluorophenyl groups as part of the cations. The crystals were obtained in addition to those of the parent halide salts. The polyhalides are formed by aerobic oxidation of the halide during the crystallization process. The corresponding crystals are recognized by their intense color.

Results and Discussion

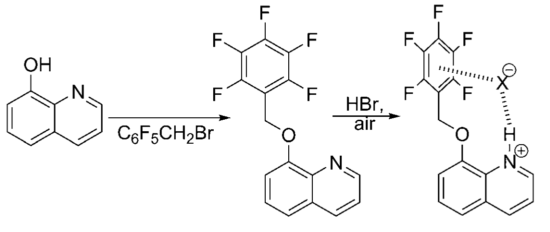
Polyhalide anions are charge-transfer adducts between a dihalide and a halide anion. They are of interest due to their reactivity in oxidation or addition reactions with organic substrates[9] or as components for organic conductors.[10] The polyhalide anions are formed by reaction of the dihalide with a corresponding halide anion. This may happen in situ by formation of the dihalide from two anions followed by aggregation with an additional anion. Most common are the trihalide anions (tribromide or triiodide), but higher-order species are also observed. The tetraiodide dianion is a rare and exotic dianion that common sense says should be unstable due to electrostatic repulsion between the two iodide anions bound to a central diiodine moiety. However, this species has been observed in some rare cases.[11] Herein, examples are described in which oligo-iodides formed in situ and in the crystal interact with electron-deficient aromatic units by anion–π interactions.

During the investigations, situations were found in which the unstable tetraiodide dianion is stabilized either by direct anion–π interaction or by anion–π complexes, which provide an ideal cavity in the crystal lattice for the stabilization of this rare dianion.

Protonated quinoline as a directing group for anion–π interactions in bromide and tribromide salts: Following earlier studies on anion-directing influences of substituents at electron-deficient aromatics, derivatives of 8-pentafluorobenzyloxyquinolinium (**1**) are introduced as new π receptors. The pentafluorophenyl moiety is attached to the 8-position of the quinoline unit by a CH_2O linker. Upon protonation of the quinoline, a conformation can be adopted in which the NH bond is directed on top of the center of the fluorinated aromatics. This should be ideal to fix an anion in this position.

Compound **1** was prepared by Williamson ether synthesis in ethanol from pentafluorobenzyl bromide and 8-hydroxyquinoline in the presence of KOH as base (Scheme 1). Diffusion of hydrogen bromide into a solution of compound **1** in toluene under air results in two kinds of crystals. Single crystals suitable for solid-state measurements were obtained for compounds **1**–**3**.

Compound **1** crystallizes from dichloromethane on slow evaporation of the solvent. The solid-state structure (Figure 1) reveals π–π stacking of the pentafluorophenyl ring and the phenol ring of the quinoline moiety of a second molecule. The intermolecular distance between the stacked ring systems is about 3.5 Å. An intramolecular angle between the pentafluorophenyl plane and the quinoline plane of 96.38° is found.



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2: X = Br
3: X = Br_3

Scheme 1. Synthesis of 8-pentafluorobenzyloxy quinoline (**1**) and the corresponding bromide (**2**) and tribromide (**3**) salts.

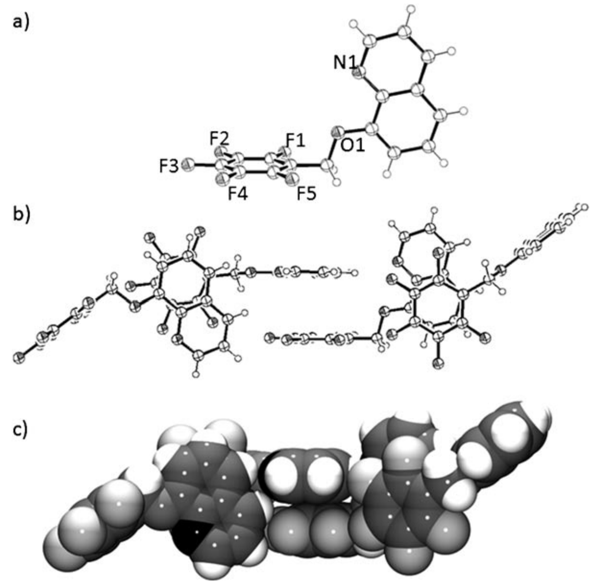

Figure 1. Structure of quinoline derivative **1** as observed in the crystal (created with ORTEP III[12], ellipsiods drawn at the 50% probability level).

Diffusion of hydrogen bromide into a solution of **1** in toluene leads to two kinds of crystals. The expected hydrogen bromide adduct **2** is obtained in form of yellow crystals containing one cocrystallized molecule of toluene. The solid-state structure of the salt (Figure 2) reveals that the NH⋯anion interaction (NH⋯Br 2.298 Å) is able to direct the anion to the top of the pentafluorophenyl unit. However, in contrast to our expectations, the anion is not located above the center of the electron-deficient ring. The distance analysis revealed only one carbon–bromide distance shorter than 4.1 Å. Therefore, the bromide shows only an η^1-type interaction (C⋯Br 3.876 Å) to one *ortho* position of the pentafluorophenyl unit. Bromide mainly interacts by CH–anion interactions (not shown in Figure 2) with toluene (CH⋯Br 2.990–3.126 Å) and with the quinoline backbone (CH⋯Br 3.509–3.624 Å).

In addition to HBr adduct **2**, hydrogen tribromide salt **3** could be obtained in the form of an orange solid by oxida-

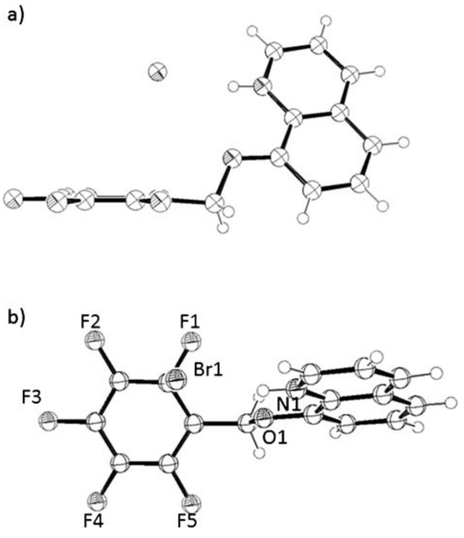

Figure 2. Two different views of part of the crystal structure of **2** (created with ORTEP III[11], ellipsiods drawn at the 50 % probability level).

tion upon crystallization. The solid-state structure (Figure 3) follows the perception that the NH···anion interaction is able to fix the anion above the π system of the pentafluorophenyl substituent. Tribromide is known in its symmetrical ([Br−Br−Br]$^-$) and unsymmetrical ([Br−Br···Br]$^-$) forms.[13] In the solid-state structure of **3**, an unsymmetrical structure is found (Br1−Br2 2.644, Br2−Br3 2.469 Å). The Br_3^- anion undergoes anion–π interactions. Analysis of the distances reveals a η^3-type interaction between Br1 and the 1-, 2-, and 3-positions of a C_6F_5 unit (C−Br1 3.596-3.917 Å). One terminus is fixed by an NH hydrogen-bonding interaction with the quinolinium moiety (NH···Br1 2.465 Å). The second terminus (Br3) interacts with the C_6F_5 moiety of another cation, which can be described as slightly shifted from η^6 (C···Br3 3.430-4.015 Å). In addition anion–π contacts are observed with the electron-deficient pyridinium unit of the quinoline. Here the electrostatic attraction between pyridinium and the anion seems to be an important contribution to the binding (C···Br2 3.671, N···Br1 3.624 Å).

In the crystal of **3**, the tribromide is located in an electron-deficient box, surrounded by aromatic π acceptors. The termini of the Br_3^- anion are capped by two pentafluorophenyl rings, and two parallel quinoline units flank the sides. An additional quinolinium group is involved in CH···anion bonds (Figure 3c, the parallel quinolinium moiety at the front is omitted for clarity). Figure 4 shows the π boxes formed in the crystal by two pentafluorophenyl and two quinolinium units, which include the tribromide anion.

A triiodide anion and a tetraiodide dianion in the crystal of a pentafluorobenzyl ammonium salt: Pentafluorobenzyldibenzylamine was obtained by treatment of dibenzyl amine with pentafluorobenzyl bromide in the presence of potassium carbonate. Crystals of **4** were obtained by diffusion of HI into a solution of the amine in toluene.

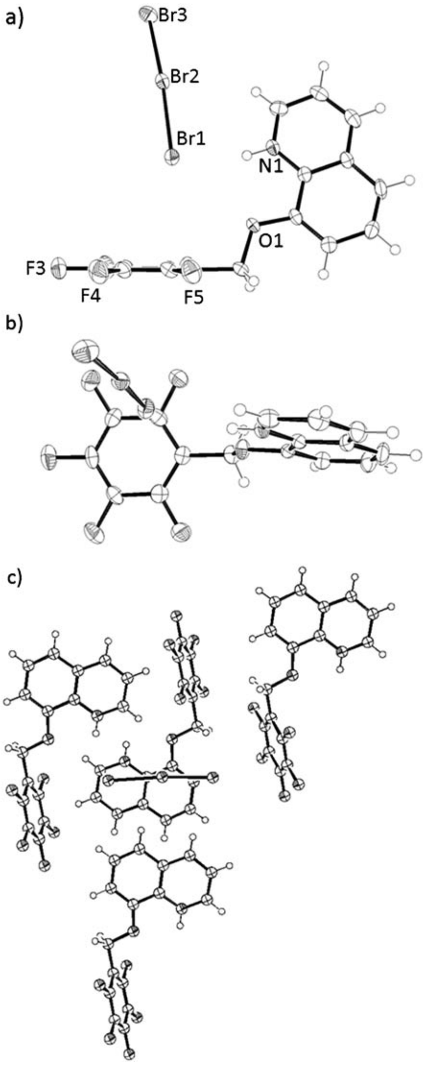

Figure 3. Different views of the solid-state structure of compound **3** (ellipsiods drawn at the 50 % probability level).

In compound **4** we observed oxidation of iodide to triiodide and to the tetraiodide dianion. Both anions are linear and interact with the lattice by CH···anion hydrogen bonds

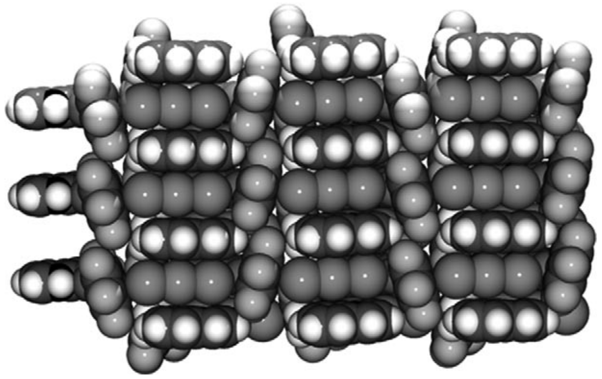

Figure 4. Part of the crystal lattice of **3** showing the inclusion of tribromide anions in boxes paneled by four π acceptors.

(Figure 5). The I–I bond lengths of the triiodide ion are 2.896 and 2.921 Å. For the tetraiodide ion, we observed bonds of $I{-}I_{internal}$ 2.762 Å and $I{-}I_{terminal} = 3.363$ Å. In addition to anion binding through CH hydrogen bonds, close contact of both anions to the pentafluorophenyl moiety is found, manifested in an anion–π interaction.

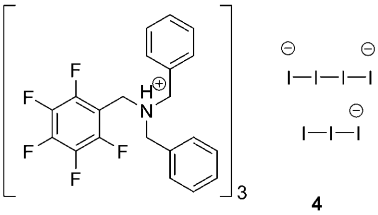

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Figure 5. Pentafluorobenzyldibenzylamonium salt **4** with I_3^- and I_4^{2-} as anions.

In compound **4**, two triiodide anions are surrounded by four ammonium cations (Figure 6) and are stabilized by CH hydrogen bonds of the benzylic and phenylic substituents (and additional CH hydrogen bonds from cocrystallized toluene). Each anion is flanked by two pentafluorophenyl moieties (C•••I 3.804-4.082 Å) with the central iodine atom located over the center of the π system. The axis of the triiodide ion is orientated in parallel to the F-C3-C6-F-axis of the perfluorinated phenyl ring.

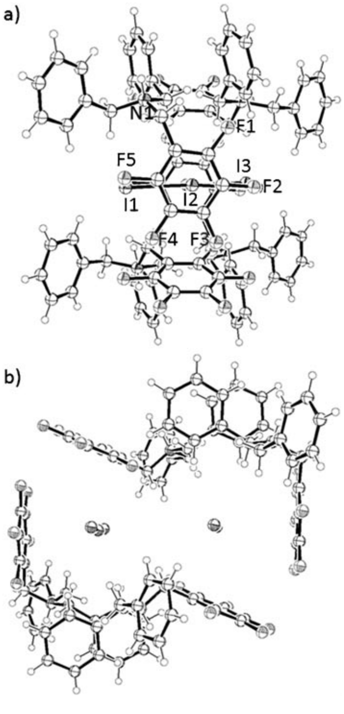


Figure 6. Part of the crystal structure of **4**. a) Top and b) side view of two triiodide anions surrounded by four cations. Each triiodide ion interacts with two electron-poor phenyl rings (ellipsiods drawn at the 50% probability level).

The tetraiodide dianion is encompassed by four ammonium cations and is stabilized by CH and NH hydrogen bonds (Figure 7). Two of the four electron-poor phenyl rings show an anion–π interaction (C•••I 3.661, 4.068 Å).

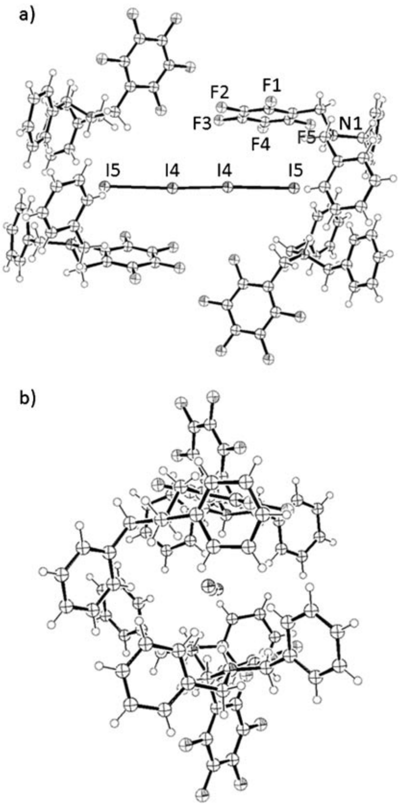
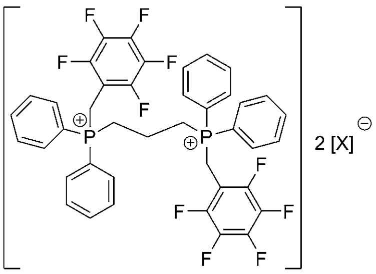


Figure 7. Two different views of the tetraiodide anion in part of the crystal structure of **4**. The termini of the linear anion are in close contact with the pentafluorophenyl units (ellipsiods drawn at the 50% probability level).

1,3-Bis(diphenylpentafluorobenzylphosphonium)propane salts with two I^- or with I^- and $^1/_2 I_4^{2-}$ as anions: Reaction of 1,3-propanylbis(diphenylphosphane) and pentafluorobenzyl iodide results in the formation of the bis-phosphonium salt, with traces of an oxidized side product as impurity. During crystallization of this salt from ethanol, colorless and red crystals were obtained.

The structural investigation of colorless crystals **5** (Figure 8) reveals that one of the two iodide anions is located nearly in the center between the planes of the pentafluorophenyl rings. This iodide ion exhibits contacts which are indicative for anion–π interactions (C•••I 4.000–5.110 Å; only two interactions are shorter than 4.1 Å). It further interacts through CH•••anion bonds with the alkyl chain (CH•••I 2.964, 2.984 Å). The iodine•••$C_{C_6F_5}$ distances seem to be quite long, but an electron-poor cavity is provided by the C_6F_5 units to host the iodide ion. The second anion shows short contacts to alkyl and phenyl hydrogen atoms.

The solid-state structure of red crystals **6** (Figure 9) shows that during the crystallization process iodine is partially oxi-



5: 2 $[X]^{\ominus}$ = 2 I^-
6: 2 $[X]^{\ominus}$ = I^- + I_4^{2-}
7: 2 $[X]^{\ominus}$ = 2 Br^-

Figure 8. Bis-phosphonium salts with two iodide (**5**) or iodide and the tetraiodide dianion (**6**) or dibromide **7**.

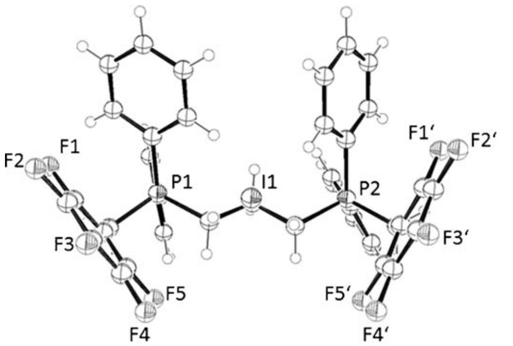


Figure 9. Part of the crystal structure of **6** showing one iodide ion centered between the two pentafluorophenyl moieties (ellipsiods drawn at the 50 % probability level).

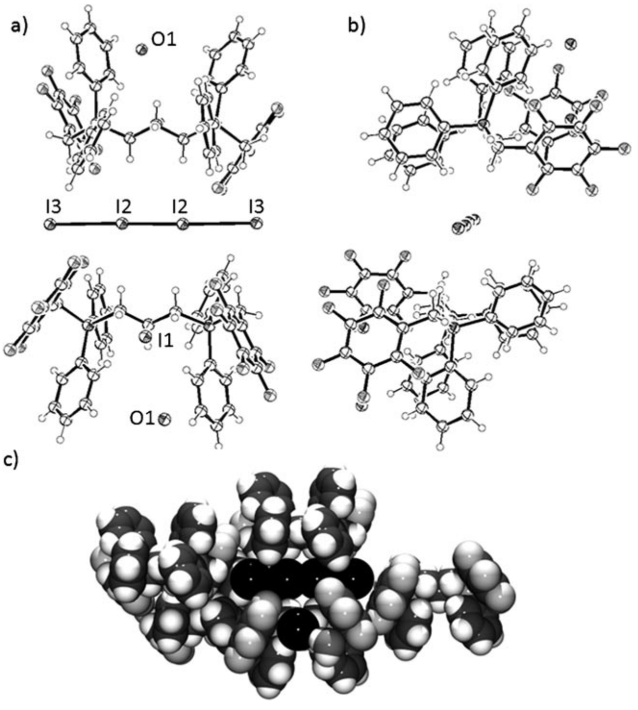


Figure 10. Different views of the dianion in the crystal of **6**, which show the linear tetraiodide anion stabilized by multiple CH hydrogen-bonding interactions (ellipsiods drawn at the 50 % probability level).

dized and the bis-phosphonium cation with one iodide and half a tetraiodide dianion is obtained. As in compound **5**, the iodide anion is located between the planes of the pentafluorophenyl rings and exhibits weak anion–π interactions ($C\cdots I$ 3.725–5.220 Å; only two interactions are shorter than 4.1 Å). CH bonds of the alkyl chains and one OH of a cocrystallized water molecule are directed towards this anion ($CH\cdots I$ 2.890, 2.990 Å).

However, the tetraiodide dianion I_4^{2-} is the most remarkable feature of the crystal structure of **6**[8] (Figure 10). The I_4^{2-} anion is positioned in a cavity, which stabilizes it through CH hydrogen bonds from the benzylic and phenylic substituents to the terminal I atoms ($CH\cdots I_{terminal}$ 2.943–3.308 Å) and between the alkyl spacer and the internal I atoms ($CH\cdots I_{internal}$ 3.251–3.271 Å).[9] The termini of the dianion are capped by pentafluorophenyl units with $I\cdots CF$ separations of 3.927–4.125 Å. Within I_4^{2-}, lengths of 2.826 (central bond) and 3.403 Å (terminal bonds) are observed.

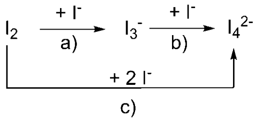
For comparison, compound **7** with two bromide anions was prepared. Only one of the anions shows an η^2 anion···π interaction ($C\cdots Br$ 3.815, 3.970 Å). In contrast to **5** or **6**, the two C_6F_5 units are orientated to opposite sides of the central diphosphonium propane moiety. Comparing **5**, **6**, and **7** reveals that the weak interactions of the diphenylpropylenediphosphonium cation with the I^- anion influence the relative orientation of the two C_6F_5 rings, creating an electron-deficient cleft to capture an I^- anion. The modulation of the crystal lattice results in an apolar tubular cavity, which in concert with CH hydrogen bonds stabilizes the tetraiodide dianion.

Computational study of I_4^{2-}: The rarely observed halogen-bonded I_4^{2-} anion in the crystal structures of **4** and **6** inspired us to perform computational studies on this species. Sæthre et al.[14] already performed some calculations on the structure and bonding of linear polyiodide compounds, which showed that the dominant intramolecular interaction in the I_4^{2-} anion is electrostatic repulsion between the terminal iodides. However, the correlation energy was omitted in their calculations[14] and, therefore, we performed additional calculations employing effective core potentials and including correlation energy by means of Møller–Plesset perturbation theory[15] to the second order (MP2).

The calculations were performed with the Gaussian 09[16] suite of programs. At the MP2/LANL2DZ[17] level of theory the molecule is very slightly bent (C_{2v}, $\sphericalangle_{I\text{-}I\text{-}I} = 179.2°$) and the lengths of the terminal and the central I—I bonds are 3.094 and 3.608 Å, respectively. A second local minimum of $D_{\infty h}$ symmetry is located only 0.03 kcal mol^{-1} above the C_2 structure. The geometries obtained at different levels of theory together with the experimental values in the solid state are listed in Table 2 of the Supporting Information, and the total energies are compiled in Table 1. Possible reaction paths giving I_4^{2-} are shown in Scheme 2.

Table 1. Total energies [Hartree] at the MP2/LANL2DZ level. Values in italics are those of the less stable linear structure; ε_0 is the zero-point energy.

	E_{tot}	ε_0	$E_{tot}+\varepsilon_0$
I_4^{2-}	44.831645	0.000727	44.830918
	44.831656	*0.000778*	*44.830878*
I_3^-	33.655768	0.000798	33.654970
I_2	22.354634	0.000407	22.354227
I^-	11.247857		



Scheme 2. Reaction paths to I_4^{2-}.

The energy changes associated with reactions a) and b) at the MP2/LANL2DZ level of theory are −33.2 and +45.1 kcal mol^{-1}, respectively. Thus, although formation of I_3^- from I_2 and I^- is exoenergetic, that of I_4^{2-} from I_3^- and I^- is significantly endoenergetic. Therefore, I_4^{2-} resides in a shallow local minimum 45.1 kcal mol^{-1} above its starting materials and is separated from them by a barrier of only 0.013 kcal mol^{-1}. The weakly bonded character of I_4^{2-} is not only reflected in the low barrier to fragmentation and the long terminal I–I bonds of 3.608 Å, but also by the results of an NBO analysis. Within the framework of this method there is neither a σ nor a π bond between the terminal iodine atoms and the central I_2 unit. Each of the terminal iodine atoms carries four lone pairs, and the only stabilization comes from an interaction of one lone pair per atom (degenerate HOMO) with the σ* orbital of the central I–I bond (LUMO). Consequently, the occupation numbers of these lone pairs are reduced to about 1.86 e whereas those of the others are essentially 2.0 e and the σ* orbital is populated by 0.28 e. This result supports Hassel's interpretation of the I_4^{2-} dianion as a charge-transfer complex of two donating iodide anions and an accepting iodine molecule.[18]

Conclusion

This crystallographic study has revealed attractive interactions between Br^-, Br_3^-, I^-, I_3^- and I_4^{2-} and electron-deficient aromatics. In **3**, the packing of the cations provides cavities for Br_3^-, which is paneled by four aromatics (terminal pentafluorophenyl and parallel quinolinium) involved in anion–π interactions. To the best of our knowledge this is the first observation of anion–π interactions involving the tribromide anion.

Salts **4** and **6** have the rare tetraiodo dianion as a component. Theoretical considerations show that the tetraiodide itself should be rather unstable towards decomposition to triiodide and iodide. In the crystal this dianion is stabilized by attractive interactions with the crystal lattice, including anion–π interactions. Thus, a first example is presented in which anion–π interactions contribute to the stabilization of an otherwise unstable species.

The presented studies and the cited references show that anion–π interaction is a dominant intermolecular force in crystals of salts with electron-deficient π systems. A challenge is to use this for host–guest interactions in solution. However, no indications were found for anion–π interactions between the ions in solution in the present case. Corresponding solution studies with related systems are currently being performed.

Experimental Section

All solvents were used after distillation without further purification. All reagents were used as received. NMR spectra were recorded in deuterochloroform by using a Varian Mercury 300 (^{1}H: 300 MHz; ^{19}F: 282 MHz), and the mass spectrometric data were taken by using a Thermo Deca XP in ESI mode. The infrared spectra were obtained in KBr by using a Perkin–Elmer FTIR spectrometer Spektrum 100 in the range of 4000–650 cm^{-1}. Elemental analyses were performed by using a CHN-O-Rapid Vario EL from Heraeus, and the melting points were measured by using a Büchi B540. XRD data were collected by using a Bruker-Nonius KappaCCD diffractometer with Apex-II detector at $T=123$ K with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Collect software[19] was used for data measurement, and DENZO-SMN[20] was used for processing. The structures were solved by direct methods with SIR2004[21] and refined by full-matrix least-squares methods using WinGX software,[22] which utilizes the SHELXL-97 module.[23] Multiscan absorption correction (SADABS[24]) was applied on all data (except for **1**). Some geometrical (DFIX and SADI) and thermal (SIMU, ISOR) parameter restraints were used to fix severely disordered molecules to be chemically reasonable in the structures. The CH hydrogen positions were calculated and refined as riding atom models with 1.2 or 1.5 times the thermal parameter of the corresponding carbon atoms. All NH and OH positions were found in the electron-density maps, and the bonds to parent atoms were fixed as idealized lengths (0.91 Å for NH, 0.84 for OH) and refined with isotropic temperature factors of 1.2 (NH) or 1.5 (OH) times the parent-atom factor.

Synthesis of 8-pentafluorobenzyloxyquinoline (1): Potassium hydroxide (108 mg, 1 equiv, 1.92 mmol) was dissolved in warm ethanol (10 mL) and hydroxyquinoline (1 equiv, 1.92 mmol, 279 mg) was added. The yellow mixture was stirred until the quinoline was completely dissolved, then pentafluorobenzyl bromide (500 mg, 1 equiv, 1.92 mmol, 290 μL) was added to give an orange mixture that turned red after 15 min. Heating to reflux for 6 h changed the color back to yellow. The mixture was cooled to RT and the white precipitate was filtered off. The colorless solid was extracted with chloroform. Crystals of **1** were grown from dichloromethane by slow evaporation of the solvent (yield: 500 mg of colorless solid, $M=325.05$ g mol^{-1}, 1.5 mmol, 81 %). M.p. 192 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=8.90$ (dd, $^3J=4.2/1.7$ Hz, 1H; H_{aryl}), 8.10 (dd, $^3J=8.4/1.7$ Hz, 1H; H_{aryl}), 7.45–7,35 (m, 3H; H_{aryl}), 7.14 (t, $^3J=4.4$ Hz, 1H; H_{aryl}), 5.35 ppm (s, 2H; $CH_2C_6F_5$); ^{19}F NMR ($CDCl_3$, 300 MHz): $\delta=-141.49$ (m, 2F; F_{ortho}), −152.87 (m, 1F; F_{para}), −161.78 ppm (m, 2F; F_{meta}); IR (KBr): $\tilde{\nu}=3430$ (w), 3366 (w), 2998 (w), 1943 (w), 2906 (w), 2803 (w), 2163 (w), 2011 (w), 1973 (w), 1710 (w), 1658 (m), 1617 (w), 1565 (m), 1521 (s), 1501 (s), 1466 (m), 1433 (m), 1373 (s), 1319 (s), 1269 (s), 1212 (m), 1180 (m), 1135 (s), 1103 (vs), 1077 (s), 1058 (s), 979 (s), 938 (vs), 884 (m), 822 (s), 799 (s), 768 (vs), 715 (s), 669 cm^{-1} (m); MS (ESI): *m/z* (%): 326.1 (100) $[M+H]^+$ ($C_{16}H_9F_5NO^+$); elemental analysis calcd (%) for $C_{16}H_8F_5NO$: C 59.09, H 2.48, N 4.31; found: C 58.71, H 2.52, N 4.27.

Synthesis of 8-pentafluorobenzyloxy quinoline hydrobromide (2): 8-Pentafluorobenzyloxyquinoline (200 mg, 1 equiv, 0.62 mmol) was dissolved in THF (10 mL), and hydrobromic acid (150 μL, 48 %, 1.4 equiv, 0.89 mmol) was added to the solution. The mixture was stirred for 1 h and then the solvent was removed under reduced pressure. The yellow solid was dried under vacuum (yield: 245 mg of yellow solid, $M=404.98$ g mol^{-1}, 0.62 mmol, quant.). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=16.68$ (brs, 1H;

NH), 9.46 (br s, 1H; H_{aryl}), 8.95 (br d, $^3J=7.8$ Hz, 1H; H_{aryl}), 8.12 (br s, 1H; H_{aryl}), 7.89 (t, $^3J=7.8$ Hz, 1H; H_{aryl}), 7.81 (d, $^3J=7.8$ Hz, 1H; H_{aryl}), 7.59 (d, $^3J=7.8$ Hz, 1H; H_{aryl}), 5.52 ppm (s, 2H; $CH_2C_6F_5$); ^{19}F NMR ($CDCl_3$, 300 MHz): $\delta=-141.12$ (m, 2F; F_{ortho}), -151.26 (m, 1F; F_{para}), -161.03 ppm (m, 2F; F_{meta}); IR (KBr): $\tilde{\nu}=3393$ (w), 3061 (w), 2995 (w), 2899 (w), 2613 (w), 2037 (w), 1936 (w), 1855 (w), 1747 (w), 1703 (w), 1662 (m), 1629 (w), 1596 (m), 1544 (s), 1507 (vs), 1387 (s), 1296 (vs), 1201 (m), 1131 (s), 1113 (s), 1055 (s), 972 (s), 937 (s), 876 (s), 821 (s), 770 (s), 751 (s), 751 (s), 666 cm^{-1} (m); MS (EI): m/z (%): 325.1 (100) $[M]^+$ ($C_{16}H_9F_5NO^+$); elemental analysis calcd (%) for $C_{16}H_8F_5NOHBr\cdot 2H_2O$: C 43.46, H 2.96, N 3.17; found: C 43.26, H 3.04, N 3.13.

Synthesis of pentafluorobenzyldibenzylamine: Potassium carbonate (1.02 g, 2 equiv, 6.14 mmol) and pentafluorobenzylbromide (470 µL, 0.800 g, 1 equiv, 3.07 mmol) were added to a solution of dibenzylamine (0.605 g, 1 equiv, 3.07 mmol) in acetonitrile (10 mL). The mixture was stirred for 24 h at RT, then the solvent was removed under reduced pressure, and the white precipitate extracted with chloroform. The solvent was removed and the white solid was recrystallized from ethanol and dried under vacuum (yield: 290 mg of white solid, $M=377.35$ g mol^{-1}, 0.77 mmol, 25%). M.p. 80°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.40$–7.20 (m, 10H; H_{aryl}), 3.73 (s, 2H; $CH_2C_6F_5$), 3.61 ppm (s, 4H; $CH_2C_6H_5$); ^{19}F NMR ($CDCl_3$, 300 MHz): $\delta=-141.31$ (m, 2F; F_{ortho}), -155.57 (m, 1F; F_{para}), -162.77 ppm (m, 2F; F_{meta}); IR (KBr): $\tilde{\nu}=3085$ (w); 3061 (w); 3031 (w); 2948 (w); 2928 (w); 2886 (w); 2811 (w); 2715 (w); 2408 (w); 2321 (w); 2060 (w); 1982 (w); 1712 (w); 1656 (w); 1600 (w); 1521 (s); 1492 (vs); 1452 (m); 1403 (w); 1377 (w); 1366 (w); 1334 (m); 1294 (m); 1271 (w); 1242 (m); 1211 (w); 1179 (w); 1161 (w); 1126 (m); 1109 (vs); 1075 (m); 1009 (vs); 975 (m); 936 (m); 913 (s); 856 (w); 832 (m); 815 (m); 745 (vs); 730 (s); 695 cm^{-1} (vs); MS (EI): m/z (%): 377.1 (59) $[M]^+$ ($C_{21}H_{16}F_5N^+$); elemental analysis calcd (%) for $C_{21}H_{16}F_5N$: C 66.84, H 4.27, N 3.71; found: C 66.83, H 4.32, N 3.74.

Synthesis of bis(phosphonium iodide) 5: 1,3-Propanylbis(diphenylphosphane) (200 mg, 1 equiv, 0.49 mmol) was dissolved in pentane (10 mL), and a solution of pentafluorobenzyl iodide (149 mg, 2 equiv, 0.98 mmol) dissolved in pentane (2 mL) was added. The mixture was stirred for 2 h at RT. The light yellow precipitate was filtered off and dried in vacuum (yield: 280 mg of white solid, $M=1027.98$ g mol^{-1}, 0.27 mmol, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.96$–7.59 (m, 10H; H_{aryl}), 4.98 (d, $^3J=13.8$ Hz, 4H; $CH_2C_6F_5$), 3.81 (br s, 4H; CH_2); 2.36 ppm (br s, 4H; CH_2); ^{19}F NMR ($CDCl_3$, 300 MHz): $\delta=-137.29$ (m, 2F; F_{ortho}), -149.98 (m, 1F; F_{para}), -158.68 ppm (m, 2F; F_{meta}); additional NMR signals arising from a minor side product were observed.

Synthesis of bis(phosphonium bromide) 7: 1,3-Propanylbis(diphenylphosphane) (100 mg, 1 equiv, 0.24 mmol) was dissolved in toluene and pentafluorobenzyl bromide (126 mg 2 equiv, 0.49 mmol) was added. The mixture was stirred for 3 h at 120°C. The white precipitate was filtered off and dried in vacuum (yield: 195 mg of white solid, $M=932.00$ g mol^{-1}, 0.21 mmol, 86%). M.p. 238°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.86$ (m, 8H; H_{aryl}), 7.68 (t, $^3J=7.3$ Hz, 4H; H_{aryl}), 7.55 (m, 8H; H_{aryl}), 5.05 (d, $^2J=13.6$ Hz, 4H; $CH_2C_6F_5$), 3.70 (br. S, 4H; CH_2), 2.45 ppm (br. S, 2H; CH_2); ^{19}F NMR ($CDCl_3$, 300 MHz): $\delta=-137.32$ (m, 4F; F_{ortho}), -150.33 (m, 2F; F_{para}), -159.12 ppm (m, 2F; F_{meta}); IR (KBr): $\tilde{\nu}=3411$ (w), 3085 (w), 3019 (w), 2843 (w), 2777 (w), 2324 (w), 2167 (w), 2108 (w), 1993 (w), 1906 (w), 1657 (w), 1616 (w), 1586 (w), 1505 (vs), 1437 (m), 1396 (w), 1308 (w), 1260 (w), 1197 (w), 1163 (w), 1114 (s), 1027 (w), 976 (vs), 866 (w), 829 (w), 801 (w), 737 (s), 687 cm^{-1} (s); MS (ESI): m/z (%): 1014.47 (100) $[MBr_3]^-$ ($C_{41}H_{30}Br_3F_{10}P_2^-$); elemental analysis calcd (%) for $C_{25}H_{17}BrF_5P\cdot H_2O$: C 51.70, H 3.39; found: C 51.48, H 3.35.

Preparation of crystals of 2–7: Compound **1** was dissolved in toluene (1 mL) in a test tube and the solution was placed in a beaker containing approximately 5 mL of hydrobromic acid (48%). Crystals were grown over three weeks under air. Crystals of **4** were grown from a solution of the free amine in toluene by diffusing hydroiodic acid into the solution. Crystals were grown from a solution of **5** in ethanol. Two kinds of crystals were obtained (colorless crystals of iodide **5** and red crystals of salt **6** with the tetraiodide dianion). Crystals of **7** were obtained by diffusion of diethyl ether into a solution in dimethylformamide.

*Crystal data for **1***: $C_{16}H_8NOF_5$; $M_r=325.23$ g mol^{-1}; tetragonal; space group $P43$; $a=7.5204(1)$, $b=7.5204(1)$, $c=23.5049(4)$ Å; $V=1329.35(3)$ Å^3; $Z=4$; $\rho_{calcd}=1.625$ g cm^{-3}; $\mu=0.150$ mm^{-1}; $F(000)=656$; crystal size $0.20\times0.12\times0.09$ mm; $\theta_{max}=25.00°$; 2297 reflections collected, 1196 unique ($R_{int}=0.0230$), 1 restraint, 208 parameters, GOF on $F^2=1.089$, final R indices for $I>2\sigma(I)$ were $R_1=0.0332$, $wR_2=0.0657$. Friedel pairs merged.

*Crystal data for **2***: $C_{16}H_9NOF_5{}^+\cdot Br^-\cdot C_7H_8$; $M_r=498.29$ g mol^{-1}; triclinic; space group $P\bar{1}$; $a=7.4444(2)$, $b=8.7250(3)$, $c=16.9105(5)$ Å; $\alpha=96.918(2)$, $\beta=93.800(2)$, $\gamma=109.434(10)°$; $V=1021.60(5)$ Å^3; $Z=2$; $\rho_{calcd}=1.620$ g cm^{-3}; $\mu=2.072$ mm^{-1}; $F(000)=500$; crystal size $0.25\times0.20\times0.16$ mm; $\theta_{max}=25.02°$; 6088 reflections collected, 3607 unique ($R_{int}=0.0286$), 1 restraint, 284 parameters, GOF on $F^2=1.025$, final R indices for $I>2\sigma(I)$ were $R_1=0.0398$, $wR_2=0.0894$.

*Crystal data for **3***: $C_{16}H_9NOF_5{}^+\cdot Br_3{}^-$; $M_r=565.97$ g mol^{-1}; triclinic; space group $P2_1/c$; $a=10.5370(4)$, $b=7.0193(2)$, $c=24.4694(8)$ Å; $\beta=98.550(2)°$; $V=1789.70(10)$ Å^3; $Z=4$; $\rho_{calcd}=2.101$ g cm^{-3}; $\mu=6.817$ mm^{-1}; $F(000)=1080$; crystal size $0.17\times0.16\times0.08$ mm; $\theta_{max}=25.00°$; 21647 reflections collected, 3154 unique ($R_{int}=0.0514$), 2 restraints, 238 parameters, GOF on $F^2=1.037$, final R indices for $I>2\sigma(I)$ were $R_1=0.0347$, $wR_2=0.0593$.

*Crystal data for **4***: $2(C_{21}H_{17}NF_5{}^+)\cdot 0.5\,I_4{}^{2-}\cdot I_3{}^-\cdot C_7H_8$; $M_r=1483.35$ g mol^{-1}; monoclinic; space group $C2/c$; $a=19.3209(3)$, $b=18.2036(3)$, $c=29.1411(4)$ Å; $\beta=93.6711(6)$; $V=10228.2(3)$ Å^3; $Z=8$; $\rho_{calcd}=1.927$ g cm^{-3}; $\mu=3.112$ mm^{-1}; $F(000)=5640$; crystal size $0.30\times0.20\times0.16$ mm; $\theta_{max}=25.02°$; 25655 reflections collected, 9021 unique ($R_{int}=0.0431$), 162 restraints, 657 parameters, GOF on $F^2=1.203$, final R indices for $I>2\sigma(I)$ were $R_1=0.0489$, $wR_2=0.1016$.

*Crystal data for **5***: $2(C_{41}H_{30}F_{10}P_2{}^{2+})\cdot 4I^-\cdot H_2O$; $M_r=2074.80$ g mol^{-1}; triclinic; space group $P\bar{1}$; $a=13.4320(2)$, $b=17.6232(3)$, $c=27.6470(5)$ Å; $\alpha=87.1980(10)$, $\beta=83.628(2)$, $\gamma=70.4250(10)°$; $V=6127.6(2)$ Å^3; $Z=3$ ($Z'=1.5$); $\rho_{calcd}=1.687$ g cm^{-3}; $\mu=1.694$ mm^{-1}; $F(000)=3042$; crystal size $0.25\times0.20\times0.13$ mm; $\theta_{max}=25.02°$; 39384 reflections collected, 21307 unique ($R_{int}=0.0532$), 316 restraints, 1602 parameters, GOF on $F^2=1.044$, final R indices for $I>2\sigma(I)$ were $R_1=0.0563$, $wR_2=0.1016$.

*Crystal data for **6***: $2(C_{41}H_{30}F_{10}P_2{}^{2+})\cdot I_4{}^{2-}\cdot 2I^-\cdot 2H_2O$; $M_r=2346.61$ g mol^{-1}; triclinic; space group $P\bar{1}$; $a=9.46480(10)$, $b=13.1523(3)$, $c=18.7539(3)$ Å; $\alpha=104.6900(10)$, $\beta=94.888(2)$, $\gamma=105.873(2)°$; $V=2141.96(6)$ Å^3; $Z=1$ ($Z'=0.5$); $\rho_{calcd}=1.819$ g cm^{-3}; $\mu=2.339$ mm^{-1}; $F(000)=1130$; crystal size $0.50\times0.10\times0.07$ mm; $\theta_{max}=25.02°$; 12658 reflections collected, 7547 unique ($R_{int}=0.0284$), 2 restraints, 521 parameters, GOF on $F^2=1.075$, final R indices for $I>2\sigma(I)$ were $R_1=0.0363$, $wR_2=0.0693$.

*Crystal data for **7***: $2(C_{41}H_{30}F_{10}P_2{}^{2+})\cdot 4Br^-\cdot 1.2(C_3H_7NO)\cdot 0.8(C_4H_{10}O)\cdot 3O$; $M_r=2063.83$ g mol^{-1}; monoclinic; space group $P2_1/c$; $a=9.7141(2)$, $b=16.7628(2)$, $c=28.9239(4)$ Å; $\beta=91.0920(10)$; $V=4708.98(13)$ Å^3; $Z=2$ ($Z'=2$); $\rho_{calcd}=1.456$ g cm^{-3}; $\mu=1.866$ mm^{-1}; $F(000)=2075$; crystal size $0.22\times0.20\times0.14$ mm; $\theta_{max}=25.02°$; 37233 reflections collected, 8294 unique ($R_{int}=0.0717$), 7 restraints, 590 parameters, GOF on $F^2=1.025$, final R indices for $I>2\sigma(I)$ were $R_1=0.0560$, $wR_2=0.1036$.

CCDC-779159 (**1**), CCDC-779160 (**2**), CCDC-779161 (**3**), CCDC-774615 (**4**), CCDC-774616 (**5**), CCDC-774617 (**6**), and CCDC-774614 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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