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Introduction

The study of an interactions, an attractive interaction between anions and electron-deficient arenes, is a very recent research topic in supramolecular chemistry. Although an ion- π interactions are observed in Nature, they have not been brought to the forefront of research earlier than in the 1990s.^{1,2} Recently, investigations on anion- π interactions have advanced significantly both computationally and experimentally.³ One of the most significant tasks in this field is the design and synthesis of receptors acting as an $n-\pi$ hosts. Anion- π interactions have a major influence on the formation of specific structures in the solid state.⁴ In solution the contribution of this interaction together with other attractive forces seems to play a role.⁵ In the crystal anion– π interactions are even able to be a driving force for the stabilization of highly reactive species.⁶ However, the anion- π interactions are elusive and difficult to study due to numerous competing other non-covalent interactions (e.g., hydrogen and halogen bonds, π - π and C-H- π interactions, *etc.*).

Fluorine is the most electronegative element and as a substituent in hexafluorobenzene induces a large positive quadrupole moment (Qzz (C_6F_6) = +9.50 B).⁷ Thus, it is not surprising that electron-deficient fluorinated arenes act as π -acceptors for a multitude of anions.⁸

Previously, we have systematically studied several anions manifesting π interactions when the pentafluorophenyl group was utilized as the π -acceptor.⁹

Perfluoro-1,1'-biphenyl and perfluoronaphthalene and their derivatives as π -acceptors for anions†

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Addition of anions to perfluorinated 1,1'-biphenyl **1** or naphthalene **2** results in a shift of the ¹⁹F NMR signals. However, any specific interaction cannot be assigned to this effect. In order to study the interaction in more detail, the salt derivatives **3** and **4** were prepared and studied by single crystal X-ray diffraction revealing weak anion– π interactions in the solid state.





In this contribution we report an extension to the anion– π hosts by introducing two new electron-deficient fluorinated aromatic motifs: perfluoro-1,1'-biphenyl (PFBP) and perfluoro-naphthalene (PFN) (Scheme 1). Solution studies of the parent compounds (1 and 2) as well as the solid state studies of their methylene DABCO bromide salts (3 and 4) are performed.

Recently, PFBP and PFN are widely used in the areas of materials science, environmental science, crystal engineering, fuel cells, as well as supramolecular chemistry.¹⁰ However, until now PFBP and PFN have not been systematically used in the studies of anion– π interactions.¹¹

Results and discussion

Solution studies with perfluoro-1,1'-biphenyl (PFBP, 1) and perfluoronaphthalene (PFN, 2) as anion receptors

The anion binding behaviour of the electron deficient **1** and **2** was investigated in $CDCl_3$ by room temperature NMR-titrations with various anions as their tetrabutylammonium (TBA) salts (TBA·Cl, TBA·Br, TBA·F, TBA·I, TBA·NO₃ and TBA·BF₄). As representative

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 $[\]dagger$ Electronic supplementary information (ESI) available: Experimental details, $^{19}{\rm F}$ NMR spectra for the titration of 1 or 2 with various tetrabutylammonium salts. Thermal ellipsoid diagrams for solved structures of 3 and 4. CCDC 1014200 and 1014201. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4nj01654h



Fig. 1 19 F NMR spectra for the titration experiment of PFBP (1) with TBA bromide (top) and tetrafluoroborate (bottom).

examples, the ¹⁹F NMR spectra for the titrations of PFBP (1) with TBA bromide (top) and tetrafluoroborate (bottom) are shown in Fig. 1. Similar spectra are observed in all titrations for both 1 and 2 (see ESI \dagger).

Addition of a small amount of the respective salt does not lead to significant shift differences in the ¹⁹F NMR spectra of the perfluorinated compounds. Addition of six equivalents or more reveals some significant high field shifting of the fluoride signals. However, this cannot be correlated with some specific binding between the aromatics and the salts; a more or less linear relation between salt addition and peak shifting is found.

Nevertheless, there are two remarkable features when comparing the two sets of spectra shown in Fig. 1 which are worth mentioning.

1. Addition of the spherical easily polarizable bromide anion results in a more pronounced shifting of the aromatic fluorine resonances compared to the shifting detected upon addition of the "less coordinating" tetrafluoroborate anion.

2. The fluoride resonance of the tetrafluoroborate anion is also dependent on the ratio between the electron deficient aromatic and the anion. Upon addition of salt (reducing the amount of PFBP *vs.* salt) a low field shift of the BF_4^- resonance is observed.

Based on the described results we conclude that upon addition of the tetrabutylammonium salts, an interaction is taking place with the perfluoroaryl derivative. Shifting in the case of the BF₄⁻ addition rules out the formation of a Meisenheimer type complex. Due to the electron deficient nature of the aromatic ring systems, interaction with the anion by anion– π interactions is feasible. However, the results obtained do not allow any final quantitative or even qualitative interpretation of the nature of the interaction in solution.

Crystal structures of the bromide salts 3 and 4

In order to get some insight into the anion– π interactions of PFBP or PFN units in the solid state, the bromide salt derivatives 3 or 4 were prepared (Scheme 2). The cationic DABCO methylene unit was chosen as a substituent according to our earlier systematic studies with related pentafluorophenyl derivatives.¹²

Bromides 3 or 4 were synthesized from the parent compounds 1 and 2 as shown in Scheme 1. In both cases a similar reaction protocol was followed. Initially the perfluoroaromatic cores were methylated twice (for 1) or once (for 2), respectively, to obtain the methyl derivatives 5 and 7. Bromination of the latter utilizing NBS in tetrachloromethane afforded the corresponding bromomethyl derivatives 6 and 8. Addition of DABCO resulted in the formation of the bromide salts 3 and 4 by nucleophilic substitution reaction.

The bromides **3** and **4** crystallize well and allow the determination of their single crystal X-ray structures. The dicationic PFBP derivative **3** was crystallized by diffusing Et_2O into the methanol solution of **3**. The salt crystallizes in the chiral space group *C*2 with only a half molecule in the asymmetric unit. The perfluorobiphenyl system has a torsional angle between the planes of the two phenyl units of 49.4(13)° (Fig. 2).

The two DABCO-methylene substituents of **3** are *anti*-orientated with respect to the biphenyl unit. The bromides are slightly disordered (92:8) over two positions and related by symmetry



Scheme 2 Preparation of 3 and 4.



Fig. 2 The structure of the bisbromide salt **3** as observed in the crystal (C: black, H: grey, Br: brown, F: yellow-green, N: blue).



Fig. 3 Side view and top view of the structure of **4** in the crystal (C: black, H: grey, Br: brown, F: yellow-green, N: blue, O: red).

(two-fold axis perpendicular to *b*). They are located close to the corresponding cationic parts interacting weakly with α -hydrogens of the DABCO unit (Br···H = 2.85, 2.88 Å, distances from the 92% component Br). Due to the torsion of the biphenyl units, the bromide anions are not located on top of the centre of the aromatic units, but in contrast to the related pentafluorophenyl derivative,¹² are situated at the rim of the perfluorobenzene ring with distances of 3.624(7), 3.640(7), 3.899(7) and 3.917(6) Å to close CF carbon atoms. This indicates an attractive anion– π interaction resulting in a η^4 -type interaction of the anion towards the tetrafluorophenyl unit. In addition weak intermolecular Br···H interactions (2.75–2.91 Å) with neighbouring DABCO moieties take place.

Crystals of the PFN-derivative **4** were obtained from methanol by slow evaporation (space group *Pbca*) as methanol solvate. The bromide ion has several weak contacts with DABCO units of adjacent cations and the cocrystallized methanol molecule is also hydrogen bonded to it ($H \cdots Br = 2.39(2)$ Å; $O \cdots Br = 3.228(4)$ Å, 173°). One of the cationic units interacts by means of $CH \cdots Br$ hydrogen bonds (2.79 and 3.06 Å) with the anion while additional attractive interactions occur by means of anion- π interactions. Again the anion is not located on top of the perfluoronaphthyl ring but is located close to the α and β carbon atom of the ring system bearing the DABCO methylene unit (η^4 -type; Br-C = 3.571(5), 3.638(4), 3.870(4) and 3.738(5) Å) (Fig. 3).

Conclusions

Herein, we demonstrated that electron deficient fluorinated biphenyl or naphthyl units can act as π -acceptors for anions. Solution studies show significant ¹⁹F NMR shifts upon addition of tetrabutylammonium salts with various anions to the parent compounds PFBP **1** or PFN **2**. The underlying interactions are not specific but might be due to anion- π interactions.

Crystal structure analyses of the salt derivatives **3** and **4** clearly indicate four positive interactions between bromide ions and the electron deficient aromatics. Due to the symmetry of the aromatic parts, a η^4 -type orientation of the bromide towards the rings is observed in both cases. The present work has some relevance in the search for anion receptors utilizing anion- π interactions as one attractive energy contribution to selectively bind negatively charged species. It shows that this concept is not restricted to singular aromatic systems (*e.g.* pentafluorophenyl) but can be found for a broad variety of electron deficient rings. In addition our work might give further evidence for possible interaction modes of fluorinated derivatives, *e.g.* in medicinal chemistry.¹³

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Notes and references

- 1 T. D. Hamilton and L. R. MacGillivray, in *Self-Assembly in Biochemistry in Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Dekker, New York, 2004, p. 1257.
- 2 (a) H.-J. Schneider, F. Werner and T. Blatter, J. Phys. Org. Chem., 1993, 6, 590; (b) D. Quiñonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa and P. M. Deyà, Angew. Chem., Int. Ed., 2002, 41, 3389; (c) P. de Hoog, P. Gamez, I. Mutikainen, U. Turpeinen and J. Reedijk, Angew. Chem., Int. Ed., 2004, 43, 5815.
- 3 (a) P. Ballester, *Struct. Bonding*, 2008, **129**, 127; (b) B. L. Schottel, H. T. Chifotides and K. R. Dunbar, *Chem. Soc. Rev.*, 2008, 37, 68;
 (c) B. P. Hay and V. S. Bryantsev, *Chem. Commun.*, 2008, 2417;
 (d) A. Frontera, P. Gamez, M. Mascal, T. J. Mooibroek and J. Reedijk, *Angew. Chem., Int. Ed.*, 2011, **50**, 9564.
- 4 See for example: (a) A. Frontera, D. Quinonero, A. Costa, P. Ballester and P. M. Deyà, New J. Chem., 2007, 31, 556; (b) S. Demeshko, S. Dechert and F. Meyer, J. Am. Chem. Soc., 2004, 126, 4508; (c) C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsa, J. M. Koomen, D. H. Russell and K. R. Dunbar, J. Am. Chem. Soc., 2005, 127, 12909; (d) B. L. Schottel, H. T. Chifotides, M. Shatruk, A. Chouai, J. Bacsa, L. M. Pérez and K. R. Dunbar, J. Am. Chem. Soc., 2006, 128, 5895; (e) S. Furkawa, T. Okubo, S. Masaoka, D. Tanaka, H. Chang and S. Kitagawa, Angew. Chem., Int. Ed., 2005, 44, 2700; (f) P. U. Maheswari, B. Modec, A. Pevec, B. Kozlevcar, C. Massera, P. Gamez and J. Reedijk, Inorg. Chem., 2006, 45, 6637; (g) H. Casellas, C. Massera, F. Buda, P. Gamez and J. Reedijk, New J. Chem., 2006, 30, 1561; (h) A. Galstyan, P. J. S. Miguel and B. Lippert, Chem. Eur. J., 2010, 16, 5577.

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- 5 E.g. (a) M. Giese, M. Albrecht, T. Krappitz, M. Peters, V. Gossen, G. Raabe, A. Valkonen and K. Rissanen, *Chem. Commun.*, 2012, 9983; (b) Z. Sun, M. Albrecht, M. Giese, F. Pan and K. Rissanen, *Synlett*, 2014, 2075; (c) A. Bretschneider, D. M. Andrada, S. Dechert, S. Meyer, R. A. Mata and F. Meyer, *Chem. Eur. J.*, 2013, **19**, 16988.
- 6 M. Müller, M. Albrecht, V. Gossen, T. Peters, A. Hoffmann,
 G. Raabe, A. Valkonen and K. Rissanen, *Chem. Eur. J.*,
 2010, 16, 12446.
- 7 C. Garau, A. Frontera, D. Quiñonero, P. Ballester, A. Costa and P. M. Deyà, *ChemPhysChem*, 2003, 4, 1344.
- 8 For selected examples of pentafluorophenyl derivatives as anion-acceptors see: (a) R. J. Götz, A. Robertazzi, I. Mutikainen, U. Turpeinen, P. Gamez and J. Reedijk, *Chem. Commun.*, 2008, 3384; (b) P. S. Lakshminarayanan, I. Ravikumar, E. Suresh and P. Ghosh, *Inorg. Chem.*, 2007, 46, 4769; (c) I. Ravikumar, P. S. Lakshminarayanan, M. Arunachalam, E. Suresh and P. Ghosh, *Dalton Trans.*, 2009, 4160; (d) O. B. Berryman, F. Hof, M. J. Hynes and D. W. Johnson, *Chem. Commun.*, 2006, 506; (e) H. Maeda, Y. Ishikawa, T. Matsuda, A. Osuka and H. Furuta, *J. Am. Chem. Soc.*, 2003, 125, 11822; (f) H. Schneider, K. M. Vogelhuber, F. Schinle and J. M. Weber, *J. Am. Chem. Soc.*, 2007, 129, 13022; (g) L. Adrienssens, G. Gil-Ramirez, A. Frontera, D. Quinonero, E. C. Escudero-Adan and P. Ballester, *J. Am. Chem. Soc.*, 2014, 136, 3208.
- 9 (a) M. Albrecht, C. Wessel, M. de Groot, K. Rissanen and A. Lüchow, J. Am. Chem. Soc., 2008, 130, 4600;
 (b) M. Albrecht, M. Müller, O. Mergel, A. Valkonen and K. Rissanen, Chem. – Eur. J., 2010, 16, 5062; (c) M. Giese,

M. Albrecht, C. Banwarth, G. Raabe, A. Valkonen and K. Rissanen, *Chem. Commun.*, 2011, 47, 8542; (*d*) M. Giese, M. Albrecht, G. Ivanova, A. Valkonen and K. Rissanen, *Supramol. Chem.*, 2012, 24, 48; (*e*) M. Giese, M. Albrecht, A. Valkonen and K. Rissanen, *Chem. Sci.*, 2015, DOI: 10.1039/C4SC02762K.

- 10 (a) A. J. Ilott, S. Palucha, A. S. Batsanov, M. R. Wilson and P. Hodgkinson, J. Am. Chem. Soc., 2010, 132, 5179; (b) M. J. Molski, M. A. Khanfar, H. Shorafa and K. Seppelt, Eur. J. Org. Chem., 2013, 3131; (c) K. Kasai and M. Fujita, Chem. - Eur. J., 2007, 13, 3089; (d) J. C. Collings, K. P. Roscoe, R. Ll. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard and T. B. Marder, New J. Chem., 2001, 25, 1410; (e) D. W. Shin, S. Y. Lee, C. H. Lee, K. Lee, C. H. Park, J. E. McGrath, M. Zhang, R. B. Moore, M. D. Lingwood, L. A. Madsen, Y. T. Kim, I. Hwang and Y. M. Lee, Macromolecules, 2013, 46, 7797; (f) Y. Chen, C. H. Lee, J. R. Rowlett and J. E. McGrath, *Polymer*, 2012, 53, 3143; (g) T. Öberg and M. S. Iqbal, Chemosphere, 2012, 87, 975; (h) A. Voege, V. A. Deimede and J. K. Kallitsis, J. Polym. Sci., Part A: Polym. Chem., 2012, 50, 207; (i) J. Kerres, F. Schoenberger, A. Chromik, T. Haering, Q. Li, J. O. Jensen, C. Pan, P. Nove and N. J. Bjerrum, Fuel Cells, 2008, 8, 175.
- 11 I. Alkorta, I. Rozas and J. Elguero, J. Am. Chem. Soc., 2002, 124, 8593.
- 12 M. Albrecht, M. Müller, O. Mergel, K. Rissanen and A. Valkonen, *Chem. Eur. J.*, 2010, **16**, 5062.
- 13 J. Wang, M. Sanchez-Rosello, J. Luis Acena, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2014, **114**, 2432.

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