MS23-P12 **Anion–π interactions in pentafluorobenzyl-substituted ammonium salts.** Arto Valkonen,[a] Michael Giese,[bc] Markus Albrecht,[b] Kari Rissanen,[a] *[a] Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, FIN-40014, Jyväskylä, Finland, [b] Institut für Organische Chemie, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany, [c] Department of Chemistry, University of British Columbia 2036 Main Mall, Vancouver, B.C. Canada V6T 1Z1*
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The chemistry of noncovalent interactions, often called supramolecular chemistry, plays a very important role in chemical and biological processes [1,2]. Interactions involving aromatic systems, such as π-π and cation-π are also found to be crucial [2]. During the past 15 years anion-π interaction between anions and electron-deficient aromatic units has been recognized as an important weak force [3]. A large number of crystal structures shows evidence for this interaction, which is rarely observed in liquid or gas phase [4]. Recently, we have been performing systematic studies, for example, on anion-π interactions of purely organic pentafluorobenzyl ammonium salts [4,5]. In this presentation we will summarize the most important findings we have observed from these systems by utilizing single crystal X-ray diffraction. Other supramolecular interactions, especially hydrogen bonding, are also involved.

[1] Steed, J., Atwood, J. L. (2009). *Supramolecular Chemistry*, 2nd ed. New York: Wiley.
[2] Salonen, L. M., Ellermann, M., Diederich, F. (2011). *Angew. Chem. Int. Ed.* **50**, 4808-4842.
[3] Robertazzi, A., Krull, F., Knapp, E.-W., Gamez, P. (2011). *CrystEngComm.* **13**, 3293-3300.
[4] Giese, M., Albrecht, M., Ivanova, G., Valkonen, A., Rissanen, K. (2012). *Supramol. Chem.* **24**, 48-55.
[5] Giese, M., Albrecht, M., Wiemer, K., Kubik, G., Valkonen, A., Rissanen K. (2012). *Eur. J. Inorg. Chem.* In the press.

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MS23-P13 **Molecular interactions in complexes of 4,4'-Dinitrobiphenyl.** Petrus van Rooyen, David Liles, Eric Modau. *Department of Chemistry, University of Pretoria, Pretoria, South Africa.*
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This study focused on the nature of molecular donor-acceptor interactions in the solid state, using spectroscopic techniques such as IR, Raman, NMR and X-ray crystallography. Complexes of para disubstituted and 4-monosubstituted biphenyl formed with 4,4'-dinitrobiphenyl (DNBP), demonstrate intense colours, from pale yellow to dark red, upon formation. These colours are dissimilar to the colour combination of the parent compounds. Typical interactions observed in such molecular complexes include đ-đ interactions, hydrogen bonding, charge transfer and van der Waals interactions. Complexes of DNBP, as the host molecule, included a variety of mono- and disubstituted biphenyl donors or guests, such as dihalo, diamino, di- and monohydroxy groups[1], as well as urea with a 1:1 host:guest ratio [2] and thiourea with a 7:6 ratio. Molecular complexes formed between DNBP with difluorobiphenyl with a 3:1 ratio and DNBP with dibromobiphenyl and diiodobiphenyl, both with 4:1 ratios, showed similar packing styles, and showed retention of the non-planar conformation of DNBP with a dihedral angle between the phenyl rings of around 35^{O}[3]. However, the dihedral angle between the phenyl rings of some dihalobiphenyls in these complexes indicate that these guests are essentially planar. The conformation for some biphenyls has also been confirmed using density functional theory (Guassian03) calculations, showing good agreement between the theoretically calculated and experimentally observed IR and Raman spectra in the solid state. It appears as if the packing of the complexes in the solid state is directed mainly by the similar packing of DNBP units in these complexes. Some of the molecular ratios for these complexes that vary, depending on the electronic properties of the donor molecules, were determined using NMR spectroscopy.

[1] Brock, C.P.; Haller, K.L. (1984). *Acta Crystallogr. Sect.C: Cryst. Struct Commun.,* **40**, 1387-.1390.
[2] Thaimattam R.; Reddy, D.S.; Feng Xue; Mak, T.C.W.; Nangia, A.; Desiraju, G.R. (1998). *J. Chem. Soc.,Perkin Trans.2*, 1783-1790.
[3] Boonstra, E.G, (1963) *Acta Cryst.* **16**, 816-823.

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