Giancarlo Terraneo[1]

[1]Politecnico di Milano, CMIC, Via Mancinelli 7, Milano, Milano, 20131, Italy, [2]ISTM-CNR, Milan, Italy, E-mail：pierangelo.metrangolo@polimi.it

Halogen atoms are typically located at the periphery of organic molecules and are thus ideally positioned to be involved in intermolecular interactions. Halogen bonding (XB) describes any interaction where halogen atoms function as electrophilic species. XB can be described by the general scheme D•••X-Y where X is the electrophilic halogen atom (Lewis acid, XB donor), D is a donor of electron density (Lewis base, XB acceptor), and Y is carbon, nitrogen, halogen, etc. (Scheme 1)[1]. The main features of the interaction will be given and the close similarity with hydrogen bonding will become apparent. Some heuristic principles will be presented in order to develop a rational crystal engineering based on XB. The potential of the interaction will be shown by useful applications in different fields spanning synthetic chemistry, material science, and bioorganic chemistry.

[1] Metrangolo P., Meyer F., Pilati T., Resnati G., Terraneo, G., Angew. Chem. Int. Ed. 2008, DOI: 10.1002/anie.200800128 (minireview).
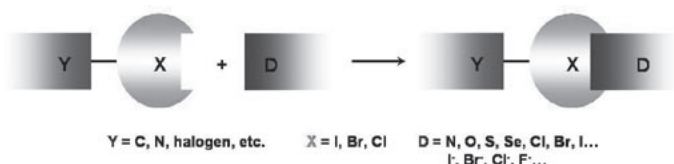
Keywords: halogen bonding, intermolecular interactions, supramolecular chemistry

MS.45.3

Structural systematic studies of fluoro(pyridinyl) benzamide derivatives

John F. Gallagher[1], Katie Donnelly[1], Alan J Lough[2]
[1]Dublin City University, School of Chemical Sciences, Glasnevin, Dublin, Dublin, 9, Ireland, [2]University of Toronto, Toronto, ON, Canada M5S 3H6, E-mail：john.gallagher@dcu.ie

We are currently studying the crystal structures of a series of Fluoro(pyridinyl)benzamides. Several isomers will be presented including the following:
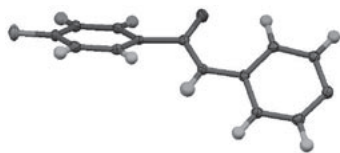Isomers (I)-(III) $C_{12}H_9FN_2O$, Monoclinic, $P2_1/c$, $Z = 4$, $T = 150K$.
(I) (4-F), $a = 5.6506(3)$, $b = 11.3882(8)$, $c = 15.4314(8)$ Å, $\beta = 95.602(3)°$ $V = 988.27(10)$Å^3, $D_x = 1.453$ Mg.m^{-3}, $R = 0.051$.
(II) (3-F), $a = 5.7537(3)$, $b = 11.2421(4)$, $c = 15.1672(7)$ Å, $\beta = 94.188(2)°$ $V = 978.45(8)$Å^3, $D_x = 1.468$ Mg.m^{-3}, $R = 0.048$.
(III) (2-F), $a = 5.9832(3)$, $b = 11.1508(5)$, $c = 14.8921(7)$ Å, $\beta = 94.986(3)°$ $V = 989.80(8)$ Å^3, $D_x = 1.451$ Mg.m^{-3}, $R = 0.044$.
An ORTEP diagram of the molecular structure of (I)

Keywords: isomers, structural systematics, fluorine compounds

MS.45.4

Crystal engineering using the thiourea moeity

Susan A Bourne[1], Nikoletta B Bathori[1], Klaus R Koch[2]
[1]University of Cape Town, Chemistry, Private Bag, Rondebosch, Cape Town, 7701, South Africa, [2]University of Stellenbosch, Matieland 7602, South Africa, E-mail：susan.bourne@uct.ac.za

Crystal engineering[1] is a form of supramolecular synthesis, where discrete molecules use molecular recognition to form supramolecular entities. We aim to identify robust H-bonding synthons that behave predictably in different chemical environments. In studies[2,3] of a variety of derivatives of monopodal and bipodal acylthioureas with varying side chains R_1, R_2 and R_3, we have observed apparently predictable intra- and intermolecular H-bond patterns (Scheme 1) In addition to the H-bonding synthons, these compounds can coordinate to metals through the thiourea moiety. This presentation will consider our own results, together with an analysis of reported structures[4] to address the following questions:
1. How robust is the H-bonding motif for differing R_2?
2. Is the same pattern observed in the monopodal and bipodal cases?
3. What is the influence of the R group or the coordinated metal on the H-bonding motif?
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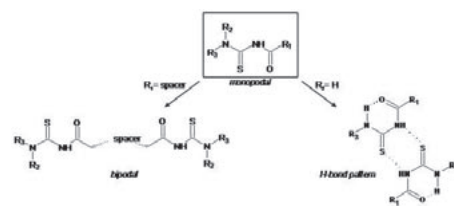
Keywords: crystal engineering, hydrogen bonding, thiourea

MS.45.5

Electrostatic complementarity: A universal theme in molecular crystal structures?

Mark A Spackman, Joshua J McKinnon, Dylan Jayatilaka
University of Western Australia, Chemistry - M313, 35 Stirling Highway, Crawley, Western Australia, 6009, Australia, E-mail：mark.spackman@uwa.edu.au

The nature of protein-protein and protein-ligand interactions has long been discussed on the basis of electrostatic complementarity, where complementary electronegative and electropositive regions are observed to pack adjacent to one-another. Although modern research in crystal engineering, crystal structure prediction and rationalization is overwhelmingly discussed in terms of specific intermolecular interactions, with special reference to the electrostatic properties of molecules, the concept of electrostatic complementarity is yet to be widely exploited in the context of molecular crystal structures. We have recently demonstrated how the graphical representation of ab initio electrostatic potentials mapped on Hirshfeld surfaces can be used to rationalize patterns of intermolecular interactions in molecular crystals, with application to small cyclic molecules such as alloxan, benzonitrile and fluorobenzene [1]. Through application to a much wider range of molecular crystals incorporating weak and strong hydrogen bonds, halogen bonds, and C-H...pi and other weak interactions, we explore the extent to which electrostatic