Poster Presentation

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Withdrawn - Intermolecular Hydrogen and Halogen Bonds in Fluorinated Benzimidazoles

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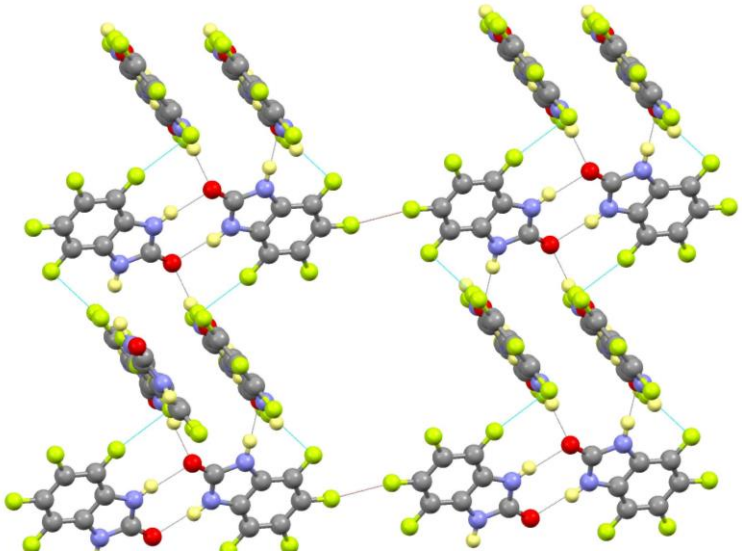
After hydrogen bonds (HB) the most studied of related weak interactions are the halogen bonds (XB). The competition between these two interactions as well as their interplay to determine the crystal packing of organic derivatives is a subject of interest. Most the studies related to XB concerns the heaviest halogen atoms, I and Br, less Cl and much less F, because the interaction energy decreases in this order. [1,2] We present here our studies on the structure of five tetrafluorinated benzazoles by X-ray crystallography and solid-state NMR, a powerful synergic mixture of techniques. The compounds are 4,5,6,7-tetrafluoro-1H-benzimidazole (1), 4,5,6,7-tetrafluoro-2-(trifluoromethyl)-1H-benzimidazole (2), 4,5,6,7-tetrafluoro-1H-benzimidazole-2(3H)-one (3), 4,5,6,7-tetrafluoro-1-methyl-1H-benzimidazole-2(3H)-one (4), and 4,5,6,7-tetrafluoro-1,3-dimethyl-1H-benzimidazole-2(3H)-one (5). As a common general feature, these compounds are quite planar due to the presence of the two aromatic rings. The existence of the methyl groups as substituent in the nitrogen atoms does not modify the planarity of the molecule. The bond distances and angles are in agreement with the expected ones for this kind of compounds. The presence of the carbonyl group induces some electronic changes in the imidazole ring that is resembled in the lengthening of the C2N3 bond distance and in a higher deviation of C2 atom from the molecular plane. Moreover, all the compounds show one or more interactions by strong linear hydrogen bonds, which lead to the formation of chains that, in some cases, can exhibit additional interactions via pi-pi and/or F•••F contacts spreading out the dimensionality of the structure in the crystal. [3] The distribution of the F•••F contacts in compounds 1-5 is similar to those of the literature and includes for 4,5,6,7-tetrafluoro-1H-benzimidazole-2(3H)-one (3) one of the shortest F•••F distances ever reported [2.596(3) Å]. Two polymorphs of compound 4 are identified.

[1] *G. Gilli, P. Gilli, The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory, IUCr Monographs on Crystallography, Oxford University Press, Oxford, 2009.,* ***[2]*** *A. Primagi, G. Cavallo, P. Metrangolo, G. Resnati, Acc. Chem. Res. 2013, 46, 2686-2695.,* ***[3]*** *C. Pérez-Medina, C. López, M. P. Cabildo, R. M. Claramunt, M. C. Torralba, M. R. Torres, I. Alkorta, J. Elguero, J. J. Mol Struct. 2012, 1022, 139-146.*



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