

SPACE CORRECTION OF FREQUENCY DISTRIBUTION FOR X-H... π INTERACTION (X = O, N, C) FOR SIX-MEMBERED AROMATIC AND CHELATE RINGS

G. A. Bogdanovic¹ A. Spasojevic-de Bire²¹VINCA Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Phys BELGRADE SERBIA 11001 YUGOSLAVIA²Laboratoire de Structures, Propriétés et Modélisation des Solides (SPMS), UMR 8580 du CNRS, Ecole Centrale Paris, Grande Voie des Vignes, 92295 Chatenay-Malabry Cedex, France

It is well known that hydrogen from X-H groups is able to grow interactions to π systems of six-membered aromatic rings [1]. Additionally, we have established very recently that π systems from chelate ring with delocalised π bonds are able to grow C-H... π interactions [2]. The simple cone correction [3] is not sufficient to answer is X-H... π interaction preferentially oriented to the center of ring or to the separate π bonds [1]. Last year, the use of an area correction [4] has given the indication that the X-H... π interaction when π is a phenyl ring is directed toward the center of the ring for C-H groups and near to the center of ring for O-H and N-H groups.

We present a new space correction used in statistical analysis of the X-H... π distribution. We have established that the hydrogen bonds are preferentially directed to the center of phenyl ring in a much more amount than with the area correction. The same behaviour appears for O-H and N-H. With this new method we are able to localize precisely where the interaction is the strongest. For example for pyridine rings X-H... π interaction is preferentially directed to the point which lies on the line which links the center of the ring and the nitrogen atom (approximately at 0.35 Å from the center of ring). For unsubstituted phenyl rings the interaction is clearly directed to the center of ring but for substituted phenyl rings (with alkyl groups or halogen atoms) the point of preferential orientation is shifted from the center of ring in the direction and at the distance which depends of the groups and their mutual positions. This new space correction is also a suitable tool for the analysis of the directionality of the X-H... π interactions for six-membered heterocyclic and chelate planar rings.

[1] G. R. Desiraju et al, The Weak Hydrogen Bond, Oxford Univ. Press. 1999

[2] G. A. Bogdanovic, et al, Eur. J. Inorg. Chem., (accepted) [3] J. Kroon et al, Nature, 1974, 248, 367 [4] Z. Ciunik et al, Chem. Commun., 2001, 703

Keywords: X-H... π INTERACTIONS, WEAK HYDROGEN BONDS, INTERMOLECULAR INTERACTIONS

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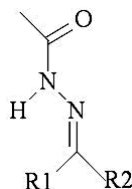
DESIGN AND CALCULATION OF HYDROGEN-BONDING PATTERNS IN ACETYLHYDRAZONES

A. Degen O. Soentgen E. Egert

Institut fuer Organische Chemie, Goethe-Universitaet Marie-Curie-Str.11 FRANKFURT 60439 GERMANY

Compounds containing both a hydrogen bond acceptor and donor group are able to crystallize as dimers as well as two- or three-dimensional networks. We are interested in finding structural conditions that selectivity force the formation of dimers. For this approach the compound class of acetylhydrazones seemed to be suitable because they show conformational flexibility and are easily available. Some acetylhydrazones with various substituents R1 and R2 were synthesized and successfully crystallized. Both dimers and chain-like arrangements were observed. Recently we have developed a strategy for calculating supramolecular structures in the gas phase within our force-field program MOMO [1]; which allows for conformational flexibility of all molecules. These calculations predicted dimers in each case and agreed well with the experimentally observed dimeric structures. We will show how the substituents R1 and R2 influence the tendency of the formation of dimers and will try to explain why non-dimeric crystal structures are formed in some cases. This leads to new suggestions for systematic variation and selection of the substituents R1 and R2.

[1] Egert; E.; Beck; H.; Bolte; M. And Gemmel; E.; MOMO; Molecular Modelling Program; V.2.00 University of Frankfurt (1999); Germany



Keywords: HYDROGEN BONDS FORCE-FIELD CALCULATIONS

CRYSTAL STRUCTURE SYNTHESIS OF HYDROGEN-BONDED METALLATE SALTS

P. Crawford T.J. Podesta A. G. Orpen

University of Bristol School of Chemistry Cantocks Close BRISTOL BS8 1TS UK

We report studies of the preparation of crystal structures with designed patterns of aggregation at a molecular level. This is done by use of a modular system in which ionic molecular tectons with hydrogen-bonding capability form 1-, 2- and 3-dimensional motifs in crystal structures. In particular $[MCl_4]^{2-}$ salts of pyridinium ions have proved useful in preparation of novel crystalline phases. Thus $[PtCl_4]^{2-}$ salts of protonated dipyridines (e.g. 2,2-, 3,3-, 4,4-bipyridine and pyridylpyridinium) have been characterised and show the same hydrogen bonded supramolecular synthon within analogous motifs. The same type of motif is also found in the saturated equivalents (e.g. in salts of $[4,4-H_2$ bipiperidine] $^{2+}$). Further aims of this work are to test the certainty with which these structures can be prepared and to exploit modularity in the expansion of available structures and their chemical diversity. Underpinning this work is development of synthetic techniques to prepare the desired compounds in the crystalline phase. To date most syntheses have been based on crystallization of the perhalometallate salts from aqueous solution, however, in some cases undesired solvent or counterion have been included in the crystal structure. Therefore we report studies of non-aqueous and solid state preparative techniques including direct reaction of pyridine hydrochlorides with anhydrous metal chlorides.

Keywords: SYNTHESIS, HYDROGEN BONDING, CRYSTAL ENGINEERING

CRYSTAL ENGINEERING OF 3-D SUPRAMOLECULAR NETWORKS WITH METALLOPORPHYRINS

Y. Diskin-Posner G.K. Patra I. Goldberg

Tel-Aviv University School of Chemistry, Sackler Faculty of Exact Sciences Ramat-Aviv TEL-AVIV 69978 ISRAEL

Three-dimensional supramolecular assemblies based on metalloporphyrins have been formulated by concerted expression of multiple interaction modes, involving axial coordination to, and π - π stacking with, the porphyrin core, as well as lateral H-bonding or lateral coordination through external metal ions. Reacting zinc-meso-tetra(4-hydroxyphenyl)porphyrin with 4,4-bipyridyl (bpy) in a 2:1 ratio led to one type of a 3-D supramolecular array. The bidentate bpy ligand binds to two porphyrin macrocycles on opposite sides to give a wheel-and-axle oligomer. These oligomers are held together by interporphyrin H-bonding, and arrange in an open three-dimensional network that consists less than 40% of the crystal volume. A simultaneous coordination polymerization in the axial direction and H-bonding in the equatorial plane is represented by the 1:1 complex of deprotonated zinc-meso-tetra(4-carboxyphenyl)porphyrin [ZnTCPP] and the 1,2-bis(4,4-dipyridinium)ethane-dibenzo-24-crown-8 cation. The resulting polyrotaxane structure is composed of layered porphyrin arrays joined together in a robust manner by the bridging ligand. Interaction of ZnTCPP with 2,7-diazapyrene and sodium ions yields a complex supramolecular architecture interconnected via specific interaction synthons in three orthogonal directions. The sodium ions link between adjacent porphyrin species by coordination to their peripheral carboxylic functions, while the diazapyrene ligand takes part in H-bonding as well as π - π stacking interactions with the porphyrin building blocks. ZnTCPP, bpy and sodium ions, were combined to form a spectacular and remarkably stable zeolite-like architecture with channels of nanometric dimensions. In the open polymeric framework, the individual metalloporphyrin units are cross-linked both axially as well as equatorially by ion-pairing, metal-ligand coordination and H-bonding.

Keywords: SUPRAMOLECULAR CHEMISTRY, SELF-ASSEMBLY, PORPHYRINS