

J.M. Ribo, J.M. McBride, S. Veintemillas-Verdaguer, *Angew. Chem. Int. Ed.* **2011**, *50*, 2359-2363.

Keywords: chirality, cluster, critical

MS.94.2

Acta Cryst. (2011) **A67**, C203

Sergeants and soldiers in two dimensions: Amplification of chirality in molecular monolayers at surfaces

Karl-Heinz Ernst, *Empa, Swiss Federal Laboratories for Materials Science and Technology, Organic Chemistry Institute, University of Zurich (Switzerland)*. E-mail: karl-heinz.ernst@empa.ch

A promising approach to study chiral molecular recognition is studying two-dimensional (2D) crystallization phenomena on well-defined surfaces via scanning tunneling microscopy (STM). We present studies on different two-dimensional chiral systems and discuss their tendency to undergo enantiomeric separation. A special surface enantiomorphism is observed via STM after adsorption of the enantiomers of a helical aromatic hydrocarbon on Cu(111). Instead of crystallization into homochiral 2D domains on the surface [1], racemic enantiomorphs are observed. In this situation, a small excess of one enantiomer is sufficient to create domains possessing single handedness throughout the entire surface layer [2]. The induction of homochirality by chiral doping has also been observed for succinic acid and achiral (*R,S*)-tartaric acid [3,4]. Our findings are explained by cooperative interactions between many chiral units, similar to the mechanism of chiral amplification observed in helical polymers and coined as "Sergeant and Soldiers" principle. Another recently observed phenomenon is single enantiomorphism due to chiral conflict. Depending on the handedness of a chiral adduct to a racemic situation suppresses one enantiomorph during crystal growth, but supports the other by forming a quasiracemic solid solution [5].

[1] R. Fasel, M. Parschau, K.-H. Ernst, *Angew. Chem. Int. Ed.* **2003**, *42*, 5178-5181. [2] R. Fasel, M. Parschau, K.-H. Ernst, *Nature* **2006**, *439*, 449-452. [3] M. Parschau, S. Romer, K.-H. Ernst, *J. Am. Chem. Soc.* **2004**, *126*, 15398-15399. [4] M. Parschau, T. Kampen, K.-H. Ernst, *Chem. Phys. Lett.* **2005**, *407*, 433-437. [5] C. Roth, D. Passerone, K.-H. Ernst, *Chem. Comm.* **2010**, *46*, 8645-8647.

Keywords: 2D crystals, chirality

MS.94.3

Acta Cryst. (2011) **A67**, C203

Facet-specific binding of amino-acid analogues on quartz

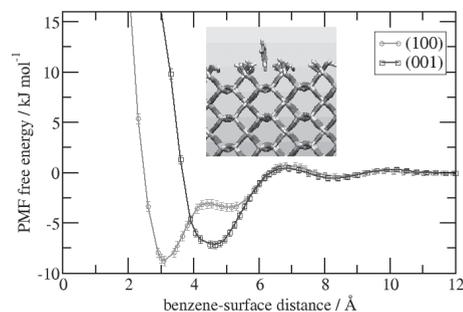
Tiffany R. Walsh,^{a,b} Louise Wright,^a ^a*Department of Chemistry, University of Warwick, Coventry, CV4 7AL, (U.K.)*. ^b*Centre for Scientific Computing, University of Warwick, Coventry, CV4 7AL, (U.K.)*. E-mail: t.walsh@warwick.ac.uk

Silica-binding peptides have a wide range of potential applications such as controlled fabrication of silica nanostructures. Quartz-binding peptides have been identified [1, 2], but their modes of binding remain less well understood [3]. As part of a programme to address the fundamentals of this problem, the free energy of adsorption of amino acid analogues on the (100), (001) and (011) hydroxylated alpha-quartz surfaces under aqueous conditions are calculated using the potential of mean constraint force method and atomistic molecular dynamics simulations. The analogues considered are methane (alanine), methanol (serine), ammonium (lysine), benzene (phenylalanine) and ethanoate (aspartic/glutamic acid). To probe the effect arising from the presence

of the linkers in the side-chains in the case of ammonium (lysine) adsorption, we also report results of simulations on butyl ammonium.

The most favourable free energies of adsorption are observed for the non-polar adsorbates methane and benzene, and also for the negatively-charged ethanoate ion, whilst the positively-charged ammonium ion showed negligible binding. The polar adsorbate methanol showed intermediate adsorption strength. Shielding of hydrophobic regions of polar and charged adsorbates by the surface are thought to contribute significantly to their surface binding, with the adsorption of methane and butyl ammonium being more favourable than that of water and ammonium respectively.

Several of these analogues show facet-specificity in their binding to these quartz surfaces. Although this energetic effect is not large for the analogues, this facet-specific adsorption may operate collectively for facet-specific peptide/biomolecule adsorption on quartz. These findings, used alongside peptide conformation data, provide a basis from which we can start to design quartz-binding peptides with controllable properties such as facet-specific binding.



[1] N. Kroger, R. Deutzmann, M. Sumper, *Science* **1999**, *286*, 1129-1132 [2] E. E. Oren, C. Tamerler, D. Sahin, M. Hnilova, U.O.S. Seker, M. Sarikaya, R. Samudrala, *Bioinformatics* **2007**, *23*, 2816-2822 [3] E.E. Oren, R. Notman, I. W. Kim, J.S. Evans, T.R. Walsh, R. Samudrala, C. Tamerler, M. Sarikaya, *Langmuir* **2010**, *26*, 11003-11009.

Keywords: selectivity, adsorption, molecular simulation

MS.94.4

Acta Cryst. (2011) **A67**, C203-C204

Noncovalent interactions of aromatic molecules

S. D. Zarić,^a G. Janjić,^b D. Sredojević,^a D. Veljković,^b J. Andrić,^a D. Ninković,^a P. Petrović,^a D. Vojislavljević,^a ^a*Department of Chemistry, University of Belgrade (Serbia)*. ^b*Institut of Chemistry, Technology and Metallurgy, University of Belgrade Njegoševa 12, Belgrade, (Serbia)*. E-mail: szaric@chem.bg.ac.rs

A characterization of noncovalent interaction of aromatic molecules is very important for crystal engineering. Aromatic molecules can form several types of noncovalent interactions, however, the best known interactions of aromatic molecules are stacking interactions with parallel alignment of the molecules. Most of the studies consider organic aromatic molecules, however, other planar molecules and fragments can also be involved in stacking interactions. We showed that a water molecule can form a parallel alignment interaction with C₆ aromatic rings [1]. Analyses of crystal structures from the Cambridge Structural Database (CSD) showed that a water molecule or one of its O-H bonds can be found parallel to the aromatic ring plane at distances typical for stacking interactions. The interaction energies obtained by *ab initio* calculations performed on model systems are as large as 2.45 kcal mol⁻¹.

In transition metal complexes planar chelate rings with delocalized π -bonds can form stacking [2]. interactions. Our results showed stacking interactions between chelate and C₆-aromatic rings in crystal

structures of square-planar transition-metal complexes. The data in the crystal structures from CSD show mutual slipped-parallel (*offset face-to-face*) orientation between chelate and C₆-aryl rings similar to the slipped-parallel orientation of two benzene rings.

Based on the fact that chelate rings with delocalized π -bonds can form stacking with C₆-aryl rings, one can anticipate that two chelate rings could form mutual stacking interaction. The evidence of chelate-chelate stacking interactions was obtained by analyzing crystal structures of square-planar transition-metal complexes from CSD [3]. The analysis showed that chelate-chelate stacking interactions occur in a large number of the crystal structures of neutral square-planar complexes.

- [1] B.D. Ostojić, G.V. Janjić, S.D. Zarić, *Chem.Comm.* **2008** (48), 6546-6548, D. Veljković, G.V. Janjić, S.D. Zarić, *Crystal Growth & Design*, submitted.
 [2] D. Sredojević, G.A. Bogdanović, Z.D. Tomić, S.D. Zarić, *CrystEngComm* **2007** 9, 793-798 [3] D.N. Sredojević, Z.D. Tomić, S.D. Zarić *Crystal Growth & Design* **2010**, 10, 3901-3908.

Keywords: intermolecular interactions, crystal structures, aromatic

MS.94.5

Acta Cryst. (2011) A67, C204

Formation and structure of fullerene and cubane based cocrystals

Éva Kováts, Gábor Bortel, Sándor Pekker, *Research Institute for Solid State Physics and Optics, Budapest, (Hungary)*. E-mail: kovats@szfki.hu

Fullerenes form a large variety of high symmetry molecular crystals with cubane molecules [1]. The basic material, C₆₀C₈H₈ has a face centered cubic crystal structure at ambient condition, with significantly expanded lattice, related to the parent fullerene structure. This cocrystal consists of separated sublattices of rotating and static components. The stabilizing factor is the strong fullerene-cubane attraction, which we explain as a molecular recognition between the convex C₆₀ and concave cubane surfaces. Although this strong shape and size recognition of the constituents allows the rotation of fullerenes, it keeps cubane in the equilibrium position and orientation. This unusual structure gives rise to a complex dynamics, called rotor-stator feature, that is different from both the orientationally ordered and the plastic crystals. As a result of this effect, the orientational ordering phase transition of fullerene-cubane takes place at the lowest temperature in all fullerene-based materials [2].

We prepared several member of this new family of heteromolecular crystals: C₇₀, C₇₆, C₇₈, C₈₄ [3] and some endohedral fullerenes also form rotor-stator phases with cubane. C₆₀ also forms cocrystals with 1,4-disubstituted cubanes. The ball-shaped fullerenes has an fcc structure with cubane, the elongated molecules compose less symmetrical structures. The different size and symmetry of the components slightly modified the rotor-stator properties. The lattice parameter depends on the sizes of fullerenes and cubane and can be predicted accurately.

The materials have rich phase diagrams and unconventional topochemistry. At elevated temperature the unimolecular isomerization of cubane results in a single phase topochemical reaction with the surrounding fullerenes. The product is a random copolymer that is stable up to high temperature.

Here we present the formation and crystal structure of the recently synthesized members of the fullerene-cubane cocrystals and discuss the effect of the molecular geometry on the crystal structure and the rotor-stator dynamics.

This work has been supported by the grant OTKA T046700.

- [1] S. Pekker, É. Kováts, G. Oszlányi, G. Bényei, G. Klupp, G. Bortel, I. Jalsovszky, E. Jakab, F. Borondics, K. Kamarás, M. Bokor, G. Kriza, K. Tompa, G. Faigel, *Nature Materials* **2005**, 4(10), 764-767. [2] G. Bortel, S. Pekker, É. Kováts, *Crystal Growth and Design* **2011**, 11(3), 865-874. [3] S. Pekker, É. Kováts, G. Oszlányi, G. Bényei, G. Klupp, G. Bortel, I. Jalsovszky, E. Jakab, F. Borondics, K. Kamarás, G. Faigel, *Physica Status Solidi b* **2006**, 243(13), 3032-3036.

Keywords: fullerene, cubane, molecular recognition

MS.95.1

Acta Cryst. (2011) A67, C204

Automating mail-in data collection at 11-BM at the APS

Brian H. Toby, *Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439 (USA)*. E-mail: toby@anl.gov

The 11-BM powder diffractometer [1] at the Argonne Advanced Photon Source is a high-resolution instrument ($\Delta Q/Q \approx 2 \times 10^{-4}$) with 12 independent analyzers [2] where a typical dataset is collected in an hour. The beamline is equipped with a robot and cryostream device, allowing completely automated data collection with temperatures of ± 200 C. The highest priority for the instrument deployment was to offer user access where samples are mailed to the beamline. This was selected, as this service was not widely available and offered the greatest availability to the potential user community.

To allow the high-throughput of the instrument to be accessed by a large number of users with mail-in access, it was necessary to automate not only the operation of the instrument, but all other aspects of the workflow, including: requests for sample mounting kits; filing of safety review forms; programming of the data collection parameters; acknowledging sample receipt; post-collection data reduction; sample storage; dissemination of data to users; sample disposal/return; and query of users for publication information [3]. This is accomplished primarily via web interfaces that offer users additional features, such as tables summarizing samples and datasets. Care is taken to provide privacy for experimental information without demanding user login with password protection. A crucial component of mail-in operation has been adoption of sample bases that regularize sample mounting and where each base has a unique barcode that can be read by the robot.

The sample management system has been sufficiently popular that when on-site data collection software was later deployed, it was requested that on-site users have the option to include their work in this database.

- [1] J. Wang *et al.*, *Rev. Sci. Instr.* **2008**, 79, 085105. [2] P.L. Lee *et al.*, *J. Synch. Rad.* **2008**, 15, 427-432. [3] B.H. Toby *et al.*, *J. Appl. Cryst.* **2009**, 42, 990-993.

Keywords: diffractometer_automation, powder_diffraction, work_process_design

MS.95.2

Acta Cryst. (2011) A67, C204-C205

Automation and efficiency in the powder structure solution by EXPO package

Angela Altomare,^a Corrado Cuocci,^a Carmelo Giacovazzo,^{a,b} Anna Moliterni,^a Rosanna Rizzi,^a ^a*Institute of Crystallography CNR, via Amendola 122/o 70126 Bari (Italy)*. ^b*Geomineralogical Department, University of Bari, via Orabona 4 70125 Bari (Italy)*. E-mail: angela.altomare@ic.cnr.it