

P08.03.05*Acta Cryst.* (2008). **A64**, C420**Monte Carlo simulations of fullerene-cubane**Bart Verberck^{1,2}, Gerrit A Vliegthart², Gerhard Gompper²¹University of Antwerp, Department of Physics, Groenenborgerlaan 171, Antwerp, Antwerp, 2020, Belgium, ²Theorie der weichen Materie und Biophysik, Institut fuer Festkoerperforschung, Forschungszentrum Juelich, 52425 Juelich, Germany, E-mail: bart.verberck@ua.ac.be

Macroscopic amounts of C₆₀.C₈H₈ (fullerene-cubane) can nowadays be synthesised [1]. By means of powder and single crystal x-ray diffraction the structure of C₆₀.C₈H₈ has been inferred to be face-centered cubic (fcc) at room temperature. The fcc phase exhibits freely rotating fullerene molecules. Below 140 K the crystal lattice is orthorhombic and the fullerene molecules adopt fixed orientations. The cubane molecules are orientationally ordered in both phases, an observation deduced from proton NMR measurements [1]. Recent x-ray scattering experiments have confirmed the existence of different solid phases of this unique molecular crystal [2]. Here we present Monte Carlo simulation results confirming a structural phase transition in C₆₀.C₈H₈. Our simulations reproduce the crystal lattices, but have in addition been designed to provide precise information about the rotational and translational motions of the fullerene and cubane molecules. In particular, we not only observe the transition from freely-rotating to non-rotating fullerenes, but we obtain the orientations of the C₆₀ molecules in the ordered (low-temperature) phase, a characteristic which has up to now not been directly obtained from experiments [1,2].

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[2] B. Verberck, V. Heresanu, S. Rouziere, J. Cambedouzou, P. Launois, E. Kovats, S. Pekker, G.A. Vliegthart, K.H. Michel, and G. Gompper, to appear in *Fuller. Nanotub. Car. N.* (2008).

Keywords: fullerenes, cubane, Monte Carlo simulations

P08.03.06*Acta Cryst.* (2008). **A64**, C420**Effect of selenium incorporation on crystal structure of arsenic sulfide (As₄S₄)**

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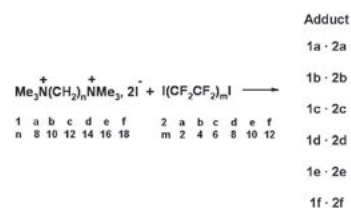
A new solid solution series of crystalline arsenic chalcogenide As₄(S,Se)₄ was prepared by sublimation method using arsenic, sulfur and selenium powder as evaporation source materials. The crystalline materials obtained by the technique exhibited a shape of an elongated prism up to approximately 3.0 mm in length. The effect of Se substitution on the As₄S₄ molecular structure has been investigated by single-crystal X-ray diffraction method and electron microprobe analysis. These products crystallized in monoclinic system with P2₁/n space group, whose molecular packing corresponds to the low-temperature phase of As₄S₄ cage-like molecule. The variation of Se concentration is continuous throughout the solid solution series, confirming a random substitution of Se for S in the molecular structure. Substitution of S in the As₄S₄ by Se to form As₄(S,Se)₄ preserves the initial As₄S₄ type configuration in the primitive monoclinic lattice, and leads to an increase of As-(S,Se) bonds and an expansion of As₄(S,Se)₄ molecules. The expansion of the molecules implies that Vegard's law is obeyed over the whole range of As₄S₄-

As₄Se₄ solid solution. Site occupancy refinements revealed that S atoms are preferentially replaced by Se atoms at the (S,Se)₂ site, whereas the substitution of S by Se is hard to occur in the (S,Se)₃ site. The a few substitution at the (S,Se)₃ site yields an extremely short As-(S,Se) bonds around (S,Se)₃ site. The difference in the As-(S,Se) bond distances brings about a deformation of the As₄(S,Se)₄ cage-like molecule. The molecular features of the anionic substitution are similar to those of the photoinduced transition of As₄S₄ molecule, which is characterized by the dissociated S₂ atom and the surviving S₃ atom during the transformation.

Keywords: As₄S₄ molecular crystal, arsenic chalcogenide, solid solution

P08.03.07*Acta Cryst.* (2008). **A64**, C420**Dynamic porous networks capable of diiodoperfluoroalkanes' mixtures separation**Pierangelo Metrangolo¹, Yvan Carcenac¹, Manu Lahtinen², Tullio Pilati³, Giuseppe Resnati^{1,3}, Kari Rissanen²¹Politecnico di Milano, CMIC, Via Mancinelli 7, Milano, Milano, 20131, Italy, ²Department of Chemistry, University of Jyväskylä, Finland, ³ISTM-CNR, Milan, Italy, E-mail: pierangelo.metrangolo@polimi.it

In this presentation we report the application of supramolecular methods and crystal engineering to the resolution of diiodoperfluoroalkanes' (DIPFAs) mixtures through selective and reversible incorporation in the crystal lattice of dynamic porous organic solids. Surprisingly, the transformation of the densely packed (non-porous) methonium iodides **1** occur rapidly and selectively in the solid state by exposition of the microcrystalline powder to the vapors of the convenient alfa,omega-DIPFAs **2**, a process that would be expected to involve surmounting a considerable energy barrier. Reminiscent of the low affinity DIPFAs have for hydrocarbons (HCs), the cations and the superanions tend to stack separately in columns. As a result of this, each superanion is surrounded by four columnar stacks of HC cations, leading to a well-defined cavity in which the DIPFA **2** is trapped thanks to strong halogen bonding. A comparison with the structure of pure decamethonium iodide **1b** suggests a 'sliding doors' mechanism to create room to the diiodoperfluorocarbon.



Keywords: halogen bonding, porous networks, supramolecular chemistry

P08.03.08*Acta Cryst.* (2008). **A64**, C420-421**Dynamic change in emission mode of ammonium anthracenedisulfonate in crystalline state**

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Efficient regulation of luminescence output induced by external stimuli is a significant issue in the development of chemical