

The work is supported by Russian Fund for Basic Research (project 10-05-00891).

[1] A.V. Li, E.N. Kotelnikova, *Zapiski Ross. Mineral. Obshch.* **2008**, 5, 48-61 (Russ.). [2] E.N. Kotelnikova, N.V. Platonova, A.V. Li, *Industrial Crystallization, Magdeburg, Germany* **2008**, BIWIC 15, 184-191. [3] Organic geochemistry / Ed.: N.B. Vassoevich, A.A. Karzev, V.A. Sokolov, *Moskow: Hedra* **1967**, 1 (Russ.). [4] Powder Diffraction File, *Intern. Centre for Diffraction Data (ICDD)*. [5] E.N. Kotelnikova, S.K. Filatov, *Crystal Chemistry of Paraffins Zhurnal "Neva"*, St. Petersburg **2002** (Russ.).

Keywords: organic, acid, isomorphism

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Structural deformations and phase transitions of normal paraffins

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Rotation of particles (atoms or molecules) around a point or an axis is a specificity of rotator crystals. Normal paraffins $n\text{-C}_n\text{H}_{2n+2}$ are classical representatives of rotator substances. This makes available to take them as examples for investigation of the rotator-crystal state, which is among the less investigated phase states of the matter. Transformation of a substance into a rotator-crystal state can be caused for instance by a heating and related to a change of the type of thermal movement of particles (atoms, molecules) due to the loss of the fixed orientation in the structure. In the case of n-paraffins, chain molecules acquire an ability of oscillator-rotator thermal motions around their axes.

Structural deformations and polymorph transitions were investigated with using of high temperature X-ray powder diffraction method (the temperature step is 0.1–0.5°C) for odd n-paraffins (*orthorhombic*) and even ones (*triclinic* and *monoclinic*) in the range of $n = 17\text{--}36$ (homological purity 97–99 %).

All the n-paraffins except of $n = 18$ transform into the low-temperature rotator-crystal state $rot.1$. Short-chain n-paraffins ($n = 17\text{--}28$) transform into the orthorhombic rotator-crystal phase $Or_{rot.1}$ [1, 2] and long-chain n-paraffins ($n = 29\text{--}36$) transform into the triclinic rotator-crystal phase $Tc_{rot.1}$ [3, 4]. The transformations of long-chain n-paraffins of $n = 27$ and 30 into the phases $Or_{rot.1}$ and $Tc_{rot.1}$ respectively run through the intermediate monoclinic rotator-crystal phase $M_{rot.1}$. The transformation of n-paraffins of $n = 33\text{--}36$ into the phase $Tc_{rot.1}$ runs through the intermediate triclinic crystal phase Tc_{cryst} . Only the "middle" (triclinic and orthorhombic) members of the n-paraffin homological members ($n = 22\text{--}26$) transform into high-temperature rotator-crystal state $rot.2$ (hexagonal phase $H_{rot.2}$). Cooling melts displayed the temperature reversibility and unreversibility of short-chain ($n = 17\text{--}28$) and long-chain ($n = 29\text{--}36$) n-paraffin transformations respectively.

The variety of the rotator crystal types (rotator-crystal states) increases owing to the crystal lattice shows the signs of both dynamic and static models as well as due to different molecules possess different character of thermal movement [1]. High temperature phase transition in long-chain n-paraffins are accompanied by lowering of crystal structure symmetry: $Or_{cryst} \rightarrow M_{rot.1}$ ($n = 27$), $Or_{cryst} \rightarrow Tc_{rot.1}$ ($n = 29$ and 31), $M_{cryst} \rightarrow Tc_{rot.1}$ ($n = 32$), $Or_{cryst} \rightarrow Tc_{cryst} \rightarrow Tc_{rot.1}$ ($n = 33$ and 35), and $M_{cryst} \rightarrow Tc_{cryst} \rightarrow Tc_{rot.1}$ ($n = 34$ and 36). The symmetry lowering proceeds due to a re-packing molecules in the n-paraffin structure. Under certain conditions, less symmetric but more dense packing can be formed.

Rotator phases possess some physical features, which are not typical for crystal substances. They are of a pronounced plasticity, which is the most important operating characteristic of n-paraffins. Eight binary

phase diagrams were plotted using data for mixtures of n-paraffins.

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[1] E.N. Kotelnikova, S.K. Filatov, *Crystal Chemistry of Paraffins, Zhurnal "Neva"*, St. Petersburg, **2002** (Russ.). [2] S.Yu. Chazhengina, E.N. Kotelnikova, I.V. Filippova, S.K. Filatov, *J. Molec. Struct.* **2003**, 647, 243-257. [3] I.A. Karetnikov, *Vestnik St. Petersburg Univ.* **2005**, 7, 2, 103-104. [4] N.V. Platonova, E.N. Kotelnikova, S.K. Filatov, *Zapiski RMO* **2006**, 3, 101-122 (Russ.).

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Ab initio direct solution from powder data lower than atomic resolution

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Direct methods work best when large numbers of well-determined reflection intensities have been collected to atomic resolution (better than 1.2Å). For a powder diffraction experiment, this situation is rarely the case. Powder diffraction patterns generally contain contributions from many overlapped reflections meaning that the condition of 'well determined' reflection intensities is not met. For moderately sized crystal structures, even with powder diffractometers of the highest angular resolution, it is impossible to obtain individual integrated intensities at atomic structural resolution.

The dual-space-based *Shake-and-Bake* procedure is one of the most successful direct methods for phasing single crystal diffraction data. A new method, termed Powder *Shake-and-Bake* [1] and implemented in the computer program *PowSnB*, addresses the handling of multiply overlapped reflections and the extension of powder diffraction data to atomic resolution via empirical estimation of the integrated intensities. *PowSnB* performs in each cycle of *SnB* iteration (i) a re-partitioning of overlapped-reflections (via partial structural information from the previous cycle), (ii) a reciprocal-space phase refinement (via the reduction of the values of a statistical minimal function), and (iii) a real-space density modification (via peak picking).

Successful *PowSnB* applications to experimental powder diffraction data lower than atomic resolution have demonstrated the power of the powder *Shake-and-Bake* method. This research was partially supported by a Knowledge Building grant from ExxonMobil Research and Engineering.

[1] Xu, H., Weeks, C. M. and Blessing, R. H. *Z. Kristallogr.* **2009**, 30, 221-226.

Keywords: powder diffraction, Shake-and-Bake, direct methods

MS10.P02

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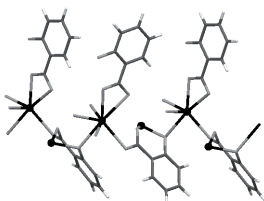
Waste-free synthesis of the metallodrug bismuth subsalicylate

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The chemistry of bismuth with salicylic acid and other carboxylic acids is an area of continuous research. Three different forms of bismuth salicylate are known, which differ in the stoichiometric ratio of bismuth and salicylic acid: the active pharmaceutical ingredient bismuth subsalicylate (**1**), the disalicylate (**2**), and the trisalicylate (**3**) involving a 1:3 stoichiometric ratio[1]. The synthesis of these from solution is complicated by the required harsh conditions and the sensitivity of the product to reaction conditions. Whereas solid-state synthetic methodologies have also been proposed,[2] their wider application is limited by issues of environmental nature and reactant toxicity. We now demonstrate the rapid, efficient and selective synthesis of into **1**, **2** and **3** by ion- and liquid-assisted grinding (ILAG)[3] directly from Bi₂O₃ and reveal the first crystal structure of a bismuth salicylate without auxiliary ligands.

Recrystallization of mechanochemically obtained **2** and **3** from N,N-dimethylformamide (DMF) yielded crystals that are isostructural with the bismuth oxo-cluster structure previously obtained from acetone by Williams *et al.*[2], with an almost identical cubooctahedral Bi₃₈ cluster, with acetone molecules coordinated to bismuth replaced by DMF. The formation of the identical bismuth core from different solvents indicates its structural robustness and supports its relevance for the activity of bismuth subsalicylate.

To further investigate this possibility, powder X-ray diffraction data was collected at the ESRF beamline ID31 for **2**. Structure solution revealed one bismuth atom and two salicylate moieties in the asymmetric unit along with a water molecule. Compound **2** is a layered material consisting of sheets held by Bi-O linkages and O-H...O hydrogen bonds. This structure is a particularly relevant addition to our understanding of the chemistry of bismuth salicylates for three reasons: *a*) it complements the existing model compounds based on discrete oligonuclear clusters involving auxiliary organic ligands; *b*) it confirms the tendency of bismuth salicylate to adopt extended structures in the absence of organic auxiliaries; *c*) demonstrates the absence of basic hydroxide or oxide species in bismuth disalicylate.



[1] (a) E.V. Timakova, T.A. Udalova, Yu.M. Yukhin Russ. *J. Inorg. Chem.* **2009**, *54*, 873. [2] P. C. Andrews, G.B. Deacon, C.M. Forsyth, P.C. Junk, I. Kumar, M. Maguire *Angew. Chem. Int. Ed.* **2006**, *45*, 5638. [3] T. Frišćić, D. G. Reid, I. Halasz, R.S. Stein, R.E. Dinnebier, M.J. Duer *Angew. Chem. Int. Ed.* **2010**, *49*, 712.

Keywords: Pharmaceutical, Bismuth, Salicylate

MS10.P03

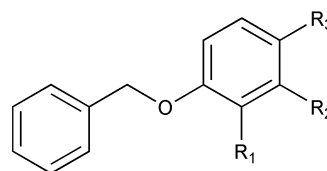
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X-ray powder diffraction study of five benzyloxy-benzene derivatives

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The benzyloxy-benzene derivatives form an important class of organic compounds with a wide range of analytical and biological applications. The structural characterization of five benzyloxy-benzene derivatives [2-benzyloxybenzoic acid (**1**), 3-benzyloxybenzoic acid (**2**), 4-benzyloxybenzoic acid (**3**), 2-benzyloxyaniline (**4**) and 3-

benzyloxyaniline (**5**)] using laboratory X-ray powder diffraction data are described, as part of our ongoing program aimed at understanding the mutual interplay between the strong and weak interactions. Crystal structures of all five compounds have been solved by direct-space approach and refined by a combination of Rietveld method and DFT based solid state geometry optimization. An investigation of close intermolecular contacts between the molecules via Hirshfeld surface analysis is also presented in order to reveal subtle differences and similarities between the five crystal structures. In the benzyloxybenzoic acids (**1-3**), the conformation of molecules depends on the position of the -C(OH)=O (carboxylic acid) group, whereas, the conformations of the two benzyloxyanilines, **4** and **5**, are quite similar. In compounds **1-3**, the carboxylic acid group with equal numbers of donors and acceptors facilitates the formation of different supramolecular assemblies. In compound **4**, the molecules are linked via C-H... π and N-H... π (arene) hydrogen bonds forming one-dimensional zig-zag chains propagating along the [100] direction. In compound **5**, aromatic π ... π stacking interactions between the phenyl rings of molecules related by inversion lead to the formation of π -stacked dimers.



- (1): R₁ = -C(=O)-OH; R₂ = H = R₃,
 (2): R₁ = H = R₃; R₂ = -C(=O)-OH,
 (3): R₁ = H = R₂; R₃ = -C(=O)-OH,
 (4): R₁ = -NH₂; R₂ = H = R₃,
 (5): R₁ = H = R₃; R₂ = -NH₂

Keywords: powder diffraction, ab-initio structure solution, Rietveld refinement

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Structural elucidation by powder synchrotron diffraction of imidate palladium complexes

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Ab initio structural elucidation of [Pd(succ)₂(NA)₂] and [Pd(sac)₂(NA)₂] (succ: succinimidate, sac: saccarinatate, NA: nicotinamide) has been made by powder X-ray diffraction.

The new complexes were obtained by treating solutions of [Pd(succ)₂(SMe₂)₂] and [Pd(sac)₂(SMe₂)₂] in acetone with nicotinamide in excess. The resulting suspension was stirred under reflux for 1 hour. The off-white solids formed were filtered and washed with water and ether. They are insoluble and it was not possible to obtain single crystals.

High resolution X-ray powder diffraction patterns were collected at the SpLine beamline (BM25A) of the Spanish CRG at the European Synchrotron Radiation Facility (ESRF, Grenoble) with a fixed wavelength of 0.8269 Å at room temperature. Powdered samples were placed inside a 0.5 mm-diameter capillary, which was rotated during exposure. Data collection was done in a continuous 2 θ -scan mode with 0.015° step and 2 sec acquisition time per point. The incoming beam was also monitored to normalize the decay of the primary beam.

The peak positions were identified using a derivative-based algorithm that is implemented in the peak search utility of the WINPLOTR software package [1]. The indexing was carried out using the commonest