

FA4-MS35-P04

X-ray diffraction studies of intercalated dichalcogenides at different temperatures. SK Imran Ali^a, Sander van Smaalen^a, Stefan Zoerb^b, Bernd Harbrecht^b, ^aLaboratory of Crystallography, University of Bayreuth, Germany, ^bDepartment of Chemistry, Philipps University, Marburg, Germany
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The crystal structures of intercalated transition metal dichalcogenides of the type 12R can be characterized by trigonal symmetry as determined by the structure from single crystal X-ray diffraction data [1]. Metal atoms of the MS₂ partial structure (M = Nb or Ta) have trigonal prismatic coordination. Cu atoms and additional M atoms may be incorporated on octahedral and tetrahedral sites in the Van der Waals gaps between layers MS₂. Here we present the structural studies of selected intercalated compounds at different temperatures between 80K and 400K using single-crystal X-ray diffraction data. The interest in these compounds is the phase transitions related to ordering of the intercalated atoms and charge-density wave transitions at different temperatures.

[1] Harbrecht B., Kreiner G., *Z. anorg. Allg. Chem.*, 572 (1989) 47-54

Keywords: X-ray diffraction, Intercalated transition metal dichalcogenides compound, Trigonal prism

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Chemical mixing and Raman hard mode spectroscopy in ferroelastic lead phosphate-arsenate: local symmetry splitting and multiscaling behavior. Ulrich Bismayer^a, Ekhard K.H. Salje^b, Tobias Beirau^a, Boriana Mihailova^a, Thomas Malcherek^a, ^aUniversität Hamburg, Germany, ^bUniversity of Cambridge, UK
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The phase transition in ferroelastic Pb₃(PO₄)₂-Pb₃(AsO₄)₂ mixed crystals shows multiscaling behaviour with two relevant length and timescales. One length scale is macroscopic and shows uniform, weakly first-order phase transformations between a rhombohedral paraphase (R $\bar{3}m$) and a monoclinic ferroelastic modification (C2/c). The second length scale is on the level of tetrahedral complexes which show monoclinic distortions at temperatures well above the macroscopic transition point. For example, in Pb₃(P_{0.43}As_{0.57}O₄)₂ the AsO₄ polyhedra show static deformation up to ca. 60 K above the deformation of the PO₄ tetrahedra. The two timescales are either short compared with the time of observation, namely the dynamic reorientation of the PO₄ tetrahedral distortion, or very long (optical birefringence, X-ray diffraction). The long timescale refers then to the quasi-static distortion of the AsO₄ tetrahedra which persists at T > T_c. These distortions appear to be uncorrelated or only weakly correlated and their random field leads to an order/disorder contribution of the ferroelastic phase transition which remains, on a phonon timescale, essentially displacive in character.

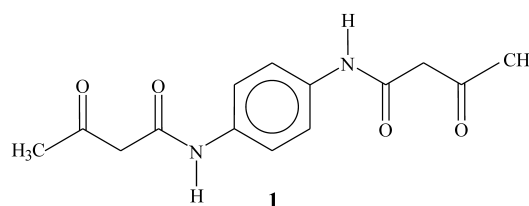
[1] Salje E.K.H., Beirau T., Mihailova B., Malcherek T., Bismayer U., *J. Phys.: Condens. Matter* 22 (2010) 045403.

Keywords: Hard Mode Raman spectroscopy, multiscaling

FA4-MS35-P06

Two polymorphs of DAEP anhydrate (C₁₄H₁₆N₂O₄) from powder diffraction data. Jürgen Brüning^a, Edith Alig^a, Jacco van de Streek^b, and Martin U. Schmidt^a
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N,N'-1,4-phenylene-bis(3-oxobutanamide) (**1**) is an industrial intermediate which is used as a coupling component in the synthesis of yellow azo pigments [1].



Two anhydrous forms could be obtained as powders by drying the dihydrate form either at 120°C (α phase) or over phosphorous pentoxide at room temperature (β phase). Single crystals of the anhydrate forms could not be obtained. The crystal structures were determined from laboratory X-ray powder diffraction data using *DASH* [2] and *TOPAS* [3]. The α phase crystallises in *P2₁/c*, *Z* = 2 with lattice parameters *a* = 16.9749(5) Å, *b* = 4.8648(1) Å, *c* = 8.5372(2) Å, \angle = 93.396(2)°, with molecules on inversion centres [4]. The β phase crystallises in *P-1* with *a* = 13.1696(4) Å, *b* = 7.9807(2) Å, *c* = 6.7519(2) Å, \angle = 105.037(1)°, \angle = 94.087(2)°, \angle = 96.075(1)°, *Z* = 2, with two symmetrically independent molecules, both on inversion centres. Thermal analyses and temperature-dependent X-ray diffraction experiments showed that the β form converts into the α form at 110°C. Both crystal structures were validated by dispersion-corrected DFT calculations using the program *GRACE* [5].

[1] Herbst, W., Hunger, K., *Industrial Organic Pigments*, 3rd ed., Wiley-VCH, Weinheim, 2004. [2] David, W.I.F., Shankland, K., Van de Streek, J., Pidcock, E., Motherwell, W.D.S., Cole, J.C., *J. Appl. Cryst.*, 2006, 39, 910-915. [3] A. A. Coelho, *TOPAS Academic*, version 4.1, 2007. [4] Brüning, J., Alig, E., Bats, J.W., Van de Streek, J., Schmidt, M.U., *Z. Kristallogr.*, 2009, 224, 593-597. [5] Neumann, M.A., Perrin, M.-A., *J. Phys. Chem.*, 2005, B109, 15531-15541.

Keywords: polymorphism, dispersion-corrected DFT calculations, structure determination from powder data

FA4-MS35-P07

Polymorphism of Pentadecanedioic Acid. T. Calvet^a, F. J. Novegil-Anleo^{a,*}, M. Font-Bardia^a, M.A. Cuevas-Diarte^a, Philippe Négrier^b and Denise Mondieig^b
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Dicarboxylic acids, $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, are interesting compounds from the structural point of view [1]. A very long one-dimensional chain can be obtained through hydrogen bond formation at both ends of the molecule. These compounds configure layered structures in the solid state, as well as most of the polymorphic phases of long-chain compounds, such as *n*-alkanes, *n*-alcohols, and *n*-fatty acids. Dicarboxylic acids exhibit interesting thermal properties and a high enthalpy of melting that make them potential candidates for their use in the field of thermal protection and energy storage.

Dimorphism was prevalent in odd carbon members of dicarboxylic acids while one form is only present for even members: α form $P2_1/c$ with $Z=4$ and β form $C2/c$ with $Z=4$. High-quality x-ray powder diffraction analyses of pentadecanedioic acid ($\text{C}_{15}\text{H}_{28}\text{O}_4$) have been carried as a function of temperature. A new form, called γ has been observed just before melting: γ form $C2/c$ with $Z=4$ at 383K. The packing arrangement of the carboxyl groups at both end of the chain is different in the three forms. From the structural point of view for γ form the distance interlayer is intermediate between α and β distances. Crystal structure of the pentadecanedioic acid is presented.

The carboxyl's group in α form shows two different angles with middle plain of the chain. The packing arrangement of α and γ forms are radically different even if the molecular conformation are *cis* in both cases.

A reversible transition from β form to γ form was observed before melting. Slurry experiments indicate that β is the most stable form at room temperature.

[1] V.R. Thalladi, M. Nüsse and R. Boese, *J. Am. Chem. Soc.*, 122, 9227-9236 (2000).

Keywords: Polymorphism, hydrogen bonds, dicarboxylic acids

FA4-MS35-P08

Polymorphism as an Obstacle for the Applicability of Methoxy-substituted Distyrylpyrazines. Alain Collas^a, Izabela Bagrowska^b, Krzysztof Aleksandrak^b, Frank Blockhuys^a, ^a*Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium*, ^b*Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 7, PL-87100 Toruń, Poland*
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Distyrylpyrazines (DSPs) are a promising class of organic semiconductors because of their superior electronic properties, such as a highly efficient emission of light and a high electron affinity [1]. Since the supramolecular structure is of great importance when rationalizing and tuning these interesting properties for the materials' use in devices such as organic LEDs, five methoxy-substituted distyrylpyrazines were synthesized and their solid-state structures were investigated; (*E,E*)-2,5-bis[2-(4-methoxyphenyl)ethenyl]pyrazine has already been subjected to a synchrotron study by Scaccianoce *et al.* [2]. For (*E,E*)-2,5-bis[2-(3,4-dimethoxyphenyl)ethenyl]pyrazine, (*E,E*)-2,5-bis[2-(3,4,5-methoxyphenyl)ethenyl]pyrazine and (*E,E*)-2,5-bis[2-(2,4,6-methoxyphenyl)ethenyl]pyr-

azine suitable crystals were grown and their supramolecular structures were analyzed. The methoxy groups are responsible for the majority of the interactions that determine the crystal packing – mostly through mutual weak hydrogen bonds and $\text{CH}\dots\pi$ interactions – although the pyrazine moiety also acts as an acceptor of weak hydrogen bonds and is involved in $\pi\dots\pi$ interactions. The structures are compared mutually as well as to their distyrylbenzene counterparts. For each of the two former compounds, two polymorphs have been found. One polymorph of (*E,E*)-2,5-bis[2-(3,4,5-methoxyphenyl)ethenyl]pyrazine proved to be light sensitive and turned out to be a good candidate for a solid-state polymerization reaction.

[1] Grimsdale A.C., Cervini R., Friend R.H., Holmes A.B., Kim S.T., Moratti S.C., *Synth. Met.*, 1997, 85, 1257. [2] Scaccianoce L., Feeder N., Teat S.J., Marseglia E.A., Grimsdale A.C., Holmes A.B., *Acta Cryst.*, 2000, C56, 1277.

Keywords: organic semiconductors, crystal packing, polymorphism

FA4-MS35-P09

Conformational flexibility of chlorpropamide molecule can generate new polymorph. T.N. Drebuschak^{a,b}, V.A. Drebuschak^{a,c}, E.V. Boldyreva^{a,b}, ^a*Novosibirsk State University, Russia*, ^b*Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia*, ^c*Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia*
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Polimorphism of drugs is of utmost importance both for pharmaceutical industry and medicine. Various molecules behave in polymorphs in different ways. For example, polymorphs of sulphathiazole differ in the framework of hydrogen bonds between molecules with similar conformations [1]. In chlorpropamide polymorphs, on the contrary, the hydrogen bonds are very similar, but the molecules have different conformations [2, 3]. There is a correlation between conformation of chlorpropamide molecule in a polymorph and its density.

We found a new phase transition of the high-temperature ϵ -chlorpropamide (metastable under normal conditions) into a new polymorph on cooling [4]. The transition is reversible. Structure of the new polymorph was solved from the single-crystal X-ray diffraction data. Space group symmetry of the polymorphs is the same, but the conformation of the molecule changes, resulting in the step-wise change in the density of chlorpropamide. Surprisingly, X-ray powder diffraction pattern of the new polymorph turned out to be nearly identical to that of stable α -chlorpropamide in the range of small angles.

Comparing the structures of chlorpropamide polymorphs, we came to the conclusion that the new polymorph is a transient point in the irreversible transition $\epsilon \rightarrow \alpha$. The state is frozen because at low temperatures molecules cannot change their conformation completely, so that every second molecular ribbon would be inverted, to give the α -form. Only the alkyl tails of the molecules turn at about 180° , but the molecular packing of the initial ϵ -form is preserved. Probably, this is an example of a new general mechanism, when the freezing of one or several degrees of freedom in conformational