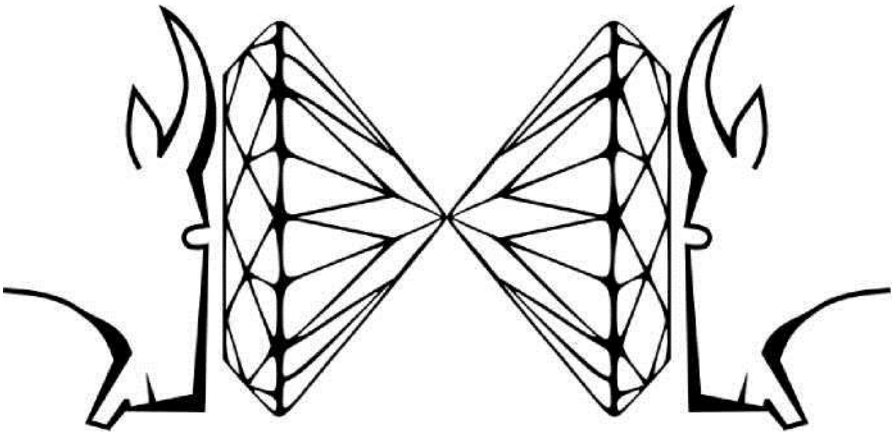
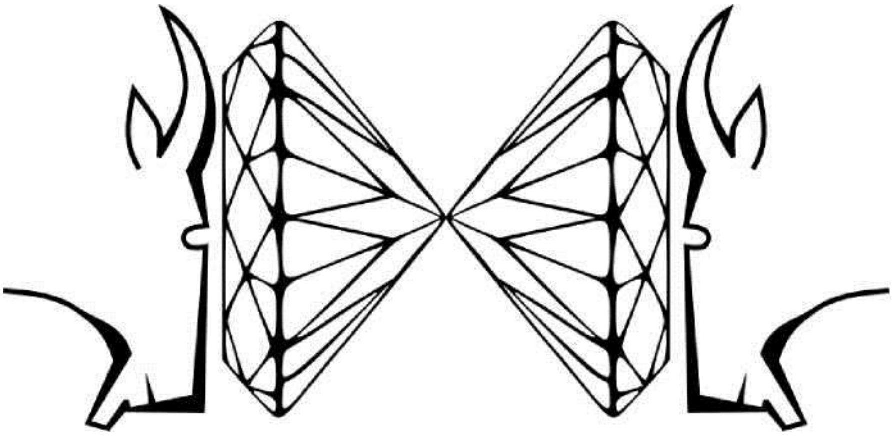


7TH FROLIC GOATS
WORKSHOP ON HIGH PRESSURE DIFFRACTION

Abstract Book

Poznań, 27-29 April 2014



Organizing Committee

Andrzej Katrusiak (chairman)
Michał Kaźmierczak (webmaster: frolicgoats.amu.edu.pl)
Anna Olejniczak
Kinga Ostrowska (abstact book editor)
Ewa Patyk
Hanna Piotrowicz
Marcin Podsiadło

Sponsors

UAM Agilent Technologies BRUKER

Welcoming address

The 7th Frolic Goats Workshop on High-Pressure Diffractometry continues the mission of disseminating the general knowledge about the application of varied thermodynamical conditions in crystal chemistry, physics and biology. Of various thermodynamical conditions for many years pressure remained most complicated experimentally and most expensive for diffraction measurements. However, after the advent of diamond-anvil cell (DAC), pressure calibration by ruby-fluorescence and 2-dimensional x-ray detectors, made the realm of high-pressure cheaper and easier accessible. Here we wish to explain the operation of the most powerful tool for modifying crystal environment. For nearly three decades it has been our aim to facilitate high-pressure diffraction experiments. They consist of several stages, involving the handling and alignment of the DAC, its loading, pressure calibration and running the diffractometer measurement in an optimal way for high-pressure experiments. Therefore we decided to organize this workshop, where the high-pressure techniques could be explained and practiced. Hence, apart from theoretical lectures, the specific tasks of handling the DAC can be performed together with experienced colleagues. But most importantly, it was our intention to create a forum of high- pressure scientists for direct exchange of experience, views and discussion.

Traditionally, the Workshop includes a social event, for establishing informal ties between the participants. This year, the young group of organizers decided to visit the recreation areas about the Malta Lake in Poznań, including the historical site of Fortress III, a small part of Russian fortifications of Stranghold Poznań (Festung Posen), ZOO, and fracts, far water races etc.

This is the Frolic Goats Workshop to be fully held in the Morasko Campus in the new Collegium Chemicum building. Finally, it is my pleasure to thank all the sponsors of the Workshop, the Faculty of Chemistry, Agilent and Bruker Polska for financial support, as well as the CrystEngComm journal of the Royal Society of Chemistry for funding a book award for the best poster.

I also thank all the members of the Organizing Committee and all teachers in the Workshop for their efforts.

Wishing you the fruitful sessions,

Andrzej Katrusiak

Scientific programme

Sunday, 27 April 2014

14^{00}	Trip to Malta Lake: visit to the New ZOO and one of Poznan Old Strongholds.

Monday, 28 April 2014

8^{30}	*Registration, room 2.57 Collegium Chemicum, Morasko Campus*
9^{00} A. Katrusiak	*Opening Ceremony*
9^{05} R. Miletich	*Advancements and experimental experiences in sXRD at non-ambient conditions*
10^{05} E. Patyk	*Pressure-induced changes in pyrimidine aggregation*
10^{25} M. Andrzejewski	Structural studies on haloimidazoles
10^{55} K. Rajewski	High-pressure structural studies on 2,4,5-tribromo and 2,4,5-trichloroimidazole
11^{15} *Coffee break*	
11^{45} J. Bąk	*Oscillation frequencies of molecules in liquids and high-pressure crystal structures*
12^{05} A. Andrada	*Structural and Electronic Properties in 2D Layered Metal Chalcogenides Under High Pressure Conditions*
12^{25} J. Marciniak	*Mandelic Acid vs the Wallach's Rule*
12^{45} W. Zieliński	*NAC – negative area compressibility in 2-Methylbenzimidazole*
13^{05} W. Cai	*Reversed Negative Linear Compressibility of a NLO organic crystal 3-methyl-4-nitropyridine N-oxide*
13^{30} M. Meyer	*HP experiments and data reduction with CrysAlis^{Pro}*
14^{15} *Poster session and lunch*	
16^{00} *Poster award ceremony and group picture*	

Tuesday, 29 April 2014

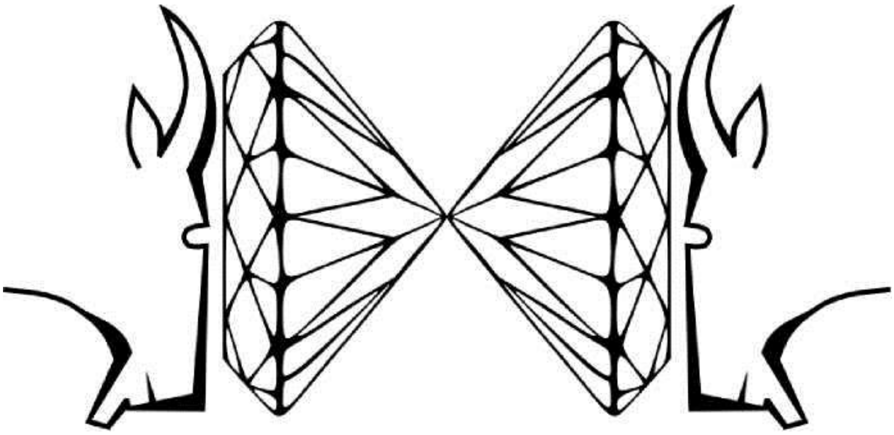
9^{00}	*Laboratory exercises: DAC construction, alignment, loading, diffraction experiment - room 2.24, Collegium Chemicum, Morasko Campus*

Contents

Lectures

Posters

Laboratory work



Lectures

Advancements and experimental experiences in sXRD at non-ambient conditions

Ronald Miletich[1]

[1]*Institut für Mineralogie und Kristallographie, Universität Wien, Althanstrasse 14, A-1090 Wien, Austria, Ronald.miletich-pawliczek@univie.ac.at*

The technique of single-crystal diffraction receives more and more attention being implemented for in-situ crystallographic research at non-ambient conditions. Aiming for up and up higher pressures and temperatures, the available sample size are restricted to a few crystallites or a single crystal which is exposed to (multi)megabar pressures and several thousands of Kelvin on using laser-heating techniques. Implementations of synchrotron micro-beam techniques and the use of new detectors with short acquisition times allow even to develop in-situ measurements which are resolved in space and time. In this context the newest advancements in high-pressure crystallography will be reported, which include the experience with new hybrid pixel detectors at synchrotron beamlines and in-house diffractometers. Within the scope of time-optimized experiments the possibilities of in-situ high-pressure-high-temperature single-crystal XRD will be shown, including the drawbacks and experimental challenges one has to consider working with HPHT devices on four-circle diffract-tometers. The results of most recent in-situ investigations on single crystals will be exemplified based on studies on the carbonate phases $CaCO_3$ and $BaMg(CO_3)_2$. Moreover we can give insight to future attempts including the use of nanopolycrystalline diamond anvils for high-quality intensity data collection aiming for an increase in quality of sXRD data and associated structure refinements form single-crystal samples.

Pressure-induced changes in pyrimidine aggregation

Ewa Patyk[1]*, Marcin Podsiadło*[1]*, Andrzej Katrusiak*[1]

[1]*Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,*
Umultowska 89b, 61-614 Poznań, Poland, ewapatyk@amu.edu.pl;

Pyrimidine, important diazine, is a precursor of many pharmaceuticals used in cancer and diabetes treatment [1]. The C-H···N and π-stacking interactions of its aromatic ring play an important role in molecular recognition [2], most relevant to drug designing. In order to obtain more information about interactions of pyrimidine molecules, their pure crystals were obtained and studied at high pressure in a Merrill-Bassett diamond-anvil cell (DAC) [3].

Our study showed that pyrimidine undergoes two phase transitions at high pressure. First takes place at 0.82 GPa and second at 1.31 GPa. This sequence of phase transitions in pyrimidine lowers its symmetry from orthorhombic $Pna2_1$ to monoclinic $P112_1/a$ and then to $P2_1/n$.

Pressure-induced phase transitions lead to displacement of molecules and result in rearrangement of C-H···N contacts and pronounced changes in molecular aggregation. Analysis of molecular aggregates present in crystals of pyrimidine shows that C-H···N interactions are gradually replaced by off-centered π-stacking.

This study was supported by the TEAM grant No. 2009-4/6 from the Foundation for Polish Science.

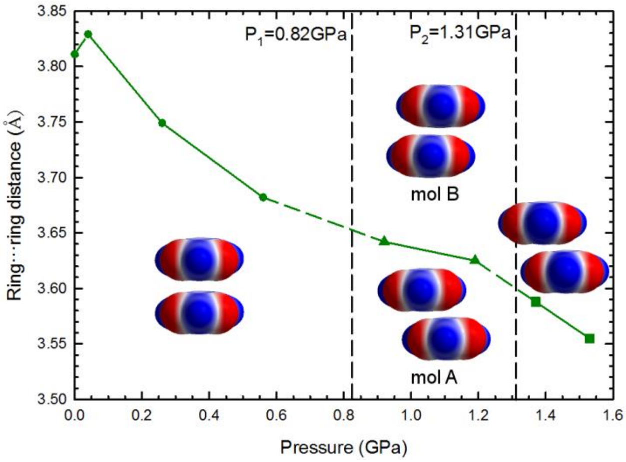


Fig. 1 Pressure dependence of ring···ring distance in pyrimidine phase I, II and III, shown as green circles, triangles and squares respectively. Vertical dashed lines mark critical pressures for phase transitions. Projection of stacked pyrimidine molecules displacement in each phase is also shown.

References

[1] Jain, K. S.; Chitre, T. S.; Miniyar, P. B.; Kathiravan, M. K.; Bendre, V. S.; Veer, V. S.; Shahane, S. R.; Shishoo, C. J. *Curr. Sci.* **90** (2006) 793-803.

[2] Tewari, A. K.; Srivastava, P.; Singh, V. P.; Singh, P.; Khanna, R. S *Res Chem Intermediate* **39** (2012) 2925-2944.

[3] Merrill, L.; Bassett, W. A. *Rev. Sci. Instrum.* **45** (1974) 290-294.

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY

ADAM MICKIEWICZ UNIVERSITY POZNAŃ

FNP Foundation for Polish Science

EUROPEAN UNION

Structural studies on haloimidazoles

Michał Andrzejewski, Jędrzej Marciniak, Kacper Rajewski, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Umultowska 89b, 61-614 Poznań, Poland, mand@amu.edu.pl

Materials with NH···N bonds may exhibit ferroelectric properties due to a switchable bond polarization. The effect was recently reported for dabco salts and halobenzimidazoles [1,2]. Halogen interactions are kind of electrostatic interactions, which can be as strong as hydrogen bonds [3]. They can be applied for designing systems like molecular conductors, optoelectronic materials [4]. Among halogen substituted imidazoles only the crystal structure of 4,5-dichloroimidazole was previously known [5]. Five novel crystal structures of double and triple halogen substituted imidazoles (by Cl, Br and I) were determined by X-ray diffraction techniques at 0.1 MPa and 296 K.

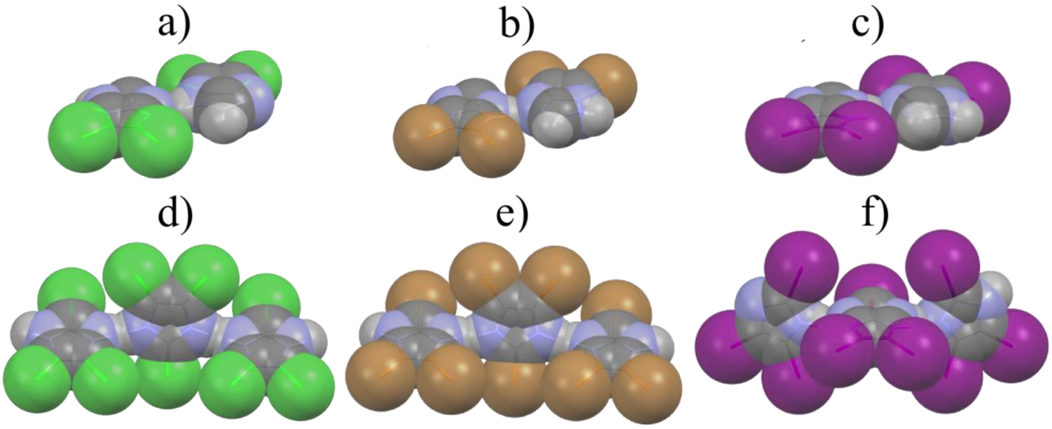


Fig. 1 a) 4,5-dichloroimidazole, b) 4,5-dibromoimidazole, c) 4,5-diiodoimidazole, d) 2,4,5-trichloroimidazole, e) 2,4,5-tribromoimidazolo, f) 2,4,5-triiodoimidazole..

References

[1] a) Szafrański, M.; Katrusiak, A.; McIntyre, G. J. Phys. Rev. Lett. 2002, 89, 5507−5510; b) Katrusiak, A.; Szafrański, M. J. Am. Chem. Soc. 2006, 128, 15775−15785.
[2] Sachio Horiuchi, Fumitaka Kagawa, Kensuke Hatahara, Kensuke Kobayashi, Reiji Kumai, Youichi Murakami Yoshinori Tokura, Nature Communications 2012, 3, Article number: 1308.
[3] Metrangolo P., Resnati G., Pilati T., Liantonio R., Meyer F. Journal of Polymer Science Part A: Polymer Chemistry 2007, 45(1):1–15.
[4] Fourmigué M., Batail P. Chem. Rev. 2004, 104(11):5379–418.
[5] CCDC ref. code: JORYIY

This study was supported by the Foundation for Polish Science, project TEAM

High-pressure structural studies on 2,4,5-tribromo and 2,4,5-trichloroimidazole

Kacper Rajewski, Jędrzej Marciniak, Michał Andrzejewski, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,

Umultowska 89b, 61-649 Poznań, Poland, kacper.rajewski@gmail.com;

Structural stability of 2,4,5-tribromoimidazole (TBI) and 2,4,5-trichloroimidazole (TClI) was investigated with X-ray diffraction techniques in a modified Merril-Bassett high-pressure diamond-anvil cell (DAC) [1]. This is a useful instrument forphase-behavior studies in searching for new polymorphs and phase transitions. High-pressure investigations allowed determining compressibility of both substances. The comparative analysis of halogen-halogen interactions supporting hydrogen bonds was done for TBI and TClI in the function of pressure. Furthermore in situ crystallization of TBI above 0.5 GPa yields a double methylated imidazole bromide hydrate. Moreover subsequent recrystallization at 1.08 GPa led to dehydration and symmetry change. Pressure induced amine methylation was recently reported for dabco hydrobomine and hydroiodine salts [2]. Alkyl derivatives of imidazole are precursors for ionic liquid [3] what consider pressure techniques as their synthesis methods.

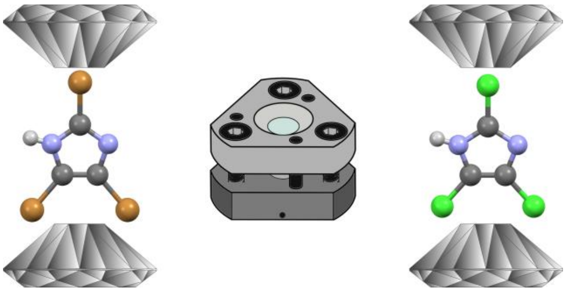


Figure 1: High-pressure investigations in a diamond-anvil cell.

Acknowledgements:

This work was supported by the Foundation for Polish Science, research project TEAM 2009-4/6.

References

[1]. L. Merrill, W. A. Bassett, Rev. Sci. Instrum., 1974, 45, 290–294.
[2]. M. Andrzejewski, A. Olejniczak, A. Katrusiak, CrystEngComm, 2012, 14, 6374-6376.
[3]. T. Welton, Chem. Rev., 1999, 99 (8), pp 2071–2084.

Oscillation frequencies of molecules in liquids and high-pressure crystal structures

Joanna Bąk[1], *Roman Gajda*[1]

[1] *Faculty of Chemistry, Warsaw University, Pasteura 1, 02-093 Warszawa, Poland,*
jbak@chem.uw.edu.pl

Crystals of 2,2-dimethylbutane (DMB) and 2,3-dimethylaniline (DMA) have been crystallised from liquid under high-pressure in Diamond Anvil Cell. Monocrystals of both compounds were obtained at 2.7 and 0.5 GPa, respectively.

High-pressure X-ray measurements were performed and confirmed that a new crystal form of DMA and DMB has been obtained. A microfocus silver X-ray source has been used to achieve the higher data completeness than in the case of Mo tube.

Simultaneously, we have measured Raman spectra for two liquid compounds - DMB and DMA and for their high pressure crystal forms. We have studied the shifts of oscillation frequencies with respect to changes of molecular environment (state of matter, pressure) and checked to what extent the isolated molecule and periodic boundary theoretical calculations are useful to reproduce this effect.

For each compound, structure optimization of isolated molecule and frequency calculations have been performed in GAUSSIAN[1] program. Moreover, series of periodic boundary theoretical calculations[2] have been performed for high-pressure crystal structures of these compounds, with the use of different constrains. In these calculations, either unit cell parameters were constrained to the values obtained from X-ray measurements conducted in given pressure conditions or were freely optimized. The DFT method with Grimme dispersion correction [3] modified as proposed by Civalleri [4] and cc-pVTZ basis set were used in periodic theoretical calculations.

Spectra obtained theoretically were compared to experimental Raman results collected for liquid (ambient pressure) and crystal (high pressure) forms of both molecules.

With increasing pressure, we observed shifts of oscillation frequencies to the higher values. The shifts of oscillation frequency values caused by changing pressure conditions, were well predicted by periodic boundary calculations performed with constrained unit-cell parameters.

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel *at al.* (2003), Gaussian 03, Revision A.1, Gaussian, Inc., Pittsburgh PA.

[2] R. Dovesi, R. Orlando, B. Civalleri, *et al.* (2008), CRYSTAL09, University of Torino, Italy.

[3] S. Grimme, (2006) *Journal of Computational Chemistry*, 27, 1787-1799.

[4] B. Civalleri, C. Zicovich-Wilson, L Valenzano, *et al* (2008), *Cryst. Eng. Comm*, 10, 405–410.

Structural and electronic properties in 2D layered metal chalcogenides under high pressure conditions

Adrián Andrada, Javier Sánchez-Benítez

Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Av. Complutense S/N, 28040 Madrid, Spain, a.andrada@ucm.es;

Layered materials are formed by stacking of two dimensional layers, commonly linked through weak interlayer interactions. Many metal chalcogenides, mainly metal transition dichalcogenides (MX_2, M = Mo, W, Nb, etc. and X = S, Se, Te) exhibit this layered structure. This kind of compounds has recently attracted much attention, due to its similitude with graphene and related systems [1] as well as their applications in nanotechnology and electronic and optoelectronic devices [2-4]. Moreover, MX_2 compounds are being widely studied under high pressure conditions. Tribology and electronic behaviour are particularly interesting issues in high pressure studies [5].

In order to characterize some of these compounds, we have been carried out several high pressure experiments, involving powder XRD, Raman spectroscopy and electrical resistivity measurements. The combination of these techniques allows us to establish a relationship between structural and electronic properties as well as their dependence with pressure. In these laminar compounds, subtle changes in the crystallographic structure may induce interesting alterations in the electronic behaviour. The most remarkable results will be shown in this contribution.

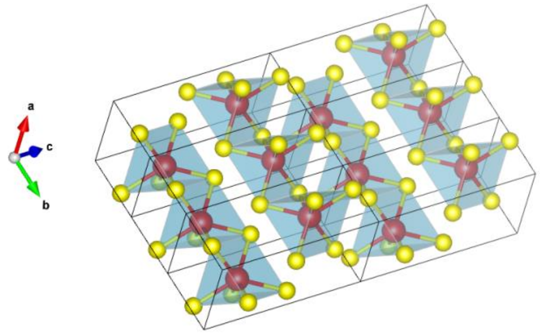


Fig. 1 Scheme of the structural polytype 2H (hexagonal symmetry, two layers per unit cell, trigonal prismatic coordination) of a typical MX_2 structure. The metal atoms (M) are shown in red, and chalcogen atoms (X) in yellow.

References

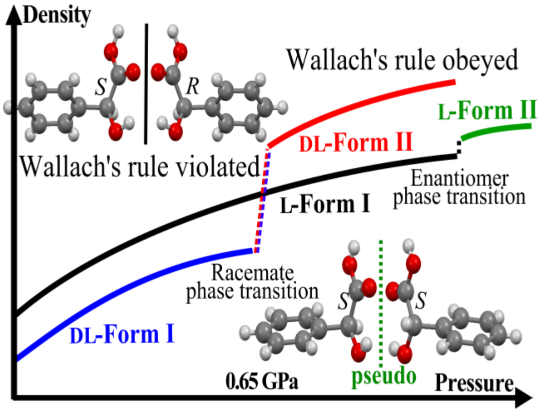
[1] Ramakrishna Matte, H.S.S. *et al.*, *Angew. Chem. Int. Ed.* **49** (2010) 4059-4062.
[2] Wang, Q.H. *et al.*, *Nature Nanotechnology* **7** (2012) 699-712.
[3] Osada, M. *et al.*, *Advanced Materials* **24** (2012) 210-228.
[4] Eda, G. *et al.*, *Nano Lett.* **11** (2011) 5111–5116.
[5] Hromadová, L. *et al.*, *Physical Review B* **87** (2013) 144105.

Mandelic acid vs the Wallach's rule

Jędrzej Marciniak, Michał Andrzejewski, Weizhao Cai, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Umultowska 89b, 61-614 Poznań, Poland, jedrzej.marciniak@amu.edu.pl;

At normal conditions, mandelic acid (MA) is an exempt from the Wallach's rule, as enantiomers L-MA and D-MA are denser than racemate DL-MA. However, the enantiomers are less compressible than the racemate, DL-MA, which additionally is anomalously compressed at the phase transition at 0.65 GPa and becomes more dense than the enantiomers. Our results exclude the possibility of resolving racemic DL-MA into enantiomers due to their higher density in a spontaneous crystallization induced by pressure up to 2.6 GPa at least. Also, the L-MA crystal undergoes an isostructural phase transition at 1.52 GPa, allowing a tighter packing of molecules mimicking a racemic arrangement. It is a general thermodynamic rule that pressure-induced phase transitions in racemates and enantiomers have the opposite effect for their densities relation and act toward or against the Wallach's rule, respectively.



References

[1] Brock, C.P.; Schweizer W.; Dunitz, J. D. On the validity of Wallach's rule: on the density and stability of racemic crystals compared with their chiral counterparts. *J. Am. Chem. Soc*. **1991**, 113 (26), 9811–9820.

[2] Jacques, J.; Collet, A.; Wilen, S. H.; Enantiomers, Racemates and Resolutions. Krieger Publishing Company: Malabar, FL. **1994**.

[3] Heo, J.; Mirkin, C. A. Pseudo-Allosteric Recognition of Mandelic Acid with an Enantioselective Coordination Complex. *Angew. Chem*. **2006**, 45 (6), 941-944.

[4] Rietveld, I. B.; Barrio, M.; Tamarit, J.-L.; Do, B.; Ceolin, R. Enantiomer Resolution by Pressure Increase: Inferences from Experimental and Topological Results for the Binary Enantiomer System (R)- and (S)-Mandelic Acid. *J. Phys. Chem. B* **2011**, 115, 14698−14703.

[5] Cai, W.; Marciniak, J.; Andrzejewski, M.; Katrusiak, A. Pressure Effect on d,l-Mandelic Acid Racemate Crystallization. *J. Phys. Chem. C* **2013**, 117, 7279-7285.

This study was supported by the Foundation for Polish Science, project TEAM

NAC – negative area compressibility in 2-Methylbenzimidazole

Witold Zieliński, *Andrzej Katrusiak*

[1]*Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,*
Umultowska 89b, 61-649 Poznań, Poland, witar6@poczta.onet.pl

Compressibility is one of the most basic properties of materials of greatest significance for their applications. Most of crystals compress in all directions at high hydrostatic pressure. The negative linear compressibility (NLC) [1] appears, when the crystal expands in one direction with increase of hydrostatic pressure is unusual, but much more unusual is the negative area compressibility (NAC) [2], when two directions expand and one direction is strongly compressed. Materials with such rare types of compressibility are sought for their possible applications in strain-eliminating composites, shock absorbers and energy transducers. Other functional properties of the materials, such as piezoelectricity, ferromagnetism, ferroelectricyty second-harmonic generation or luminescence, make their applicability even wider. Here we present unique properties of 2-Methylbenzimidazole (2MeBzIm) high-pressure phase β which exhibit very unusual effect of NAC unlike Benzimidazole (BzIm) [3] which differ from 2-MeBzIm only by methyl group in C2 position. Mechanism of discontinuous compression of BzIm and continuous compression of 2MeBzIm (Fig.1) in two analogues compounds will be discused.

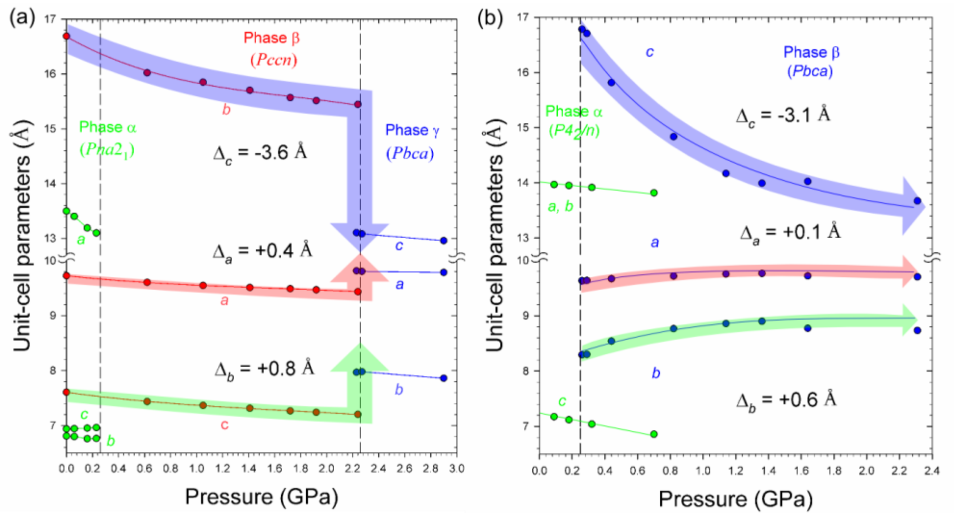


Fig. 1 Compression of unit-cell dimensions in (a) BzIm and (b) 2MeBzIm.

References

[1] Li W., Probert M. R., Kosa M., Bennett T. D., Thirumurugan A., Burwood R. P., Parinello M., Howard J. A. K., Cheetham A. K. *J. Am. Chem. Soc.* **134** (2012), 11940–11943.

[2] Baughman R. H., Stafstrom S., Cui C., Dantas S. O. *Science* **279** (1998), 1522-1524.

[3] Zielinski W., Katrusiak A. *Cryst. Growth Des.* 13 (2013) 696-700.

This study was supported by the Foundation for Polish Science, project TEAM

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY
ADAM MICKIEWICZ UNIVERSITY POZNAŃ
FNP
Foundation for Polish Science
EUROPEAN UNION

Reversed Negative Linear Compressibility of a NLO organic crystal 3-methyl-4-nitropyridine *N*-oxide

Weizhao Cai[1], *Jiangang He*[2], *Wei, Li*[3] *and Andrzej Katrusiak*[2]

[1]*Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland, wzhcai@gmail.com;* [2]*School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853,USA;* [3]*Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 0FS, UK.*

The organic crystal 3-methyl-4-nitropyridine *N*-oxide (POM) (Fig. 1) has been studied intensively in the last decades, owning to its strong second-harmonic generation response [1]. Indirect Brillouin scattering measurement revealed that POM exhibits strong negative linear compressibility (NLC) behaviour along its crystallographic *b* axis [2, 3]. By combining of variable-temperature and variable high-pressure single crystal diffraction measurements, we find POM crystal exhibits strong NLC and large positive thermal expansion. The anomalous NLC feature reversed at 120 MPa, induced by the collapse of CH···O bonded supramolecular framework and subtle rotations of the nitro group (-NO_2). The initial compression of the weak supramolecular network in the molecular POM crystal is analogues to the hydrostatic responses of the framework crystals with much stronger cohesion forces. Density functional theory (DFT) calculations show that both the subtle conformational distortions and the crystal compression modify the second-harmonic generation (SHG) efficiency of POM.

W.C. and A.K. acknowledge the financial support from the Foundation for Polish Science project, TEAM grant 2009-4/6. W.L. is grateful to the European Research Council for financial support.

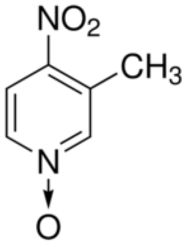


Fig. 1. The molecular structure of POM

References

[1] Zyss, J.; Chemla, D. S.; Nicoud, J. F. *J. Chem. Phys.* 74 (1981) 4800-4811.
[2] Sapriel, J.; Hierle, R.; Zyss, J.; Boissier, M. *Appl. Phys.Lett.* 55 (1989) 2594-2596.
[3] Baughman, R. H.; Stafström, S.; Cui, C.; Dantas, S. O. *Science 279(*1998) 1522-1524.

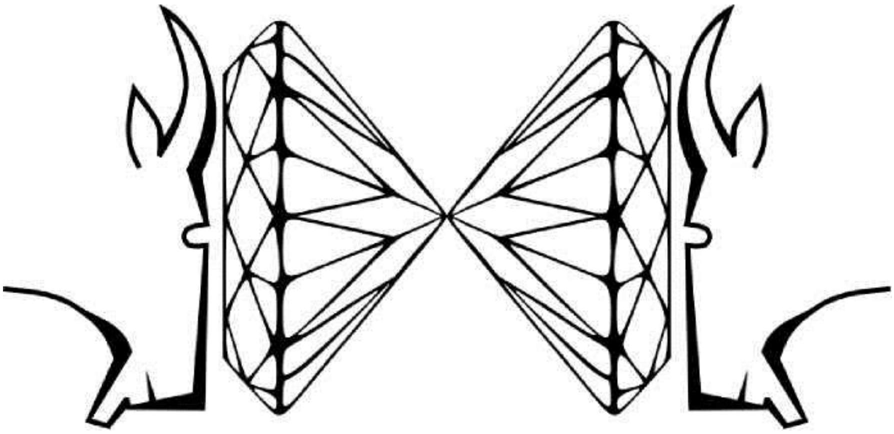
HP experiments and data reduction with CrysAlis^{Pro}

Mathias Meyer[1]

[1]*Department Agilent Technologies Poland Sp. z o. o., Ul. Szarskiego 3, PL-54-609 Wrocław, Poland, Tel.: +48 71 78 086 17, Fax: +48 71 78 086 64, mathias.meyer@agilent.com*

Version 171.37 of CrysAlis^{Pro} gives an extended support of HP experimentation and data reduction. The talk will comment on the setup of an HP experiment, sample screening and pre-experimenting. It will discuss the HP strategies. The instrument video feature can be used to gather sample shape information and the size of the gasket hole. The new Ewald^{Pro} reciprocal space viewer simplifies the way how to obtain unit cells from HP experiments. New options in data reduction (dc proffit) help to obtain even better HP data then before. At the post-processing step CrysAlis^{Pro} now interfaces with Ross Angle's program Absorb for HP cell corrections and allows seamless correction with empirical methods as well. Version 171.37 also supports the new S2 generation of Agilent's CCD cameras. Their technical features with respect to HP experiments will be discussed.

Finally some comments on synchrotron experimentation are made.



Posters

Halogen-halogen bond assisted cocrystal formation in iodinated imidazoles

Michał Andrzejewski, Kacper Rajewski, Jędrzej Marciniak, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Umultowska 89b, 61-614 Poznań, Poland, mand@amu.edu.pl

Cocrystals formation is one of the most important challenge for crystal engineering, design of pharmaceuticals in particular [1]. Halogen-halogen interactions which can be as strong as hydrogen bonds may force a creation of new architectures and arrangements in organic molecular crystals. Iodination of imidazole can result in formation of cocrystals as a by-product after a partial substitution of an imidazole ring [2]. This effect was not observed during neither chlorination nor bromination. A new cocrystal of 2,4-diiodoimidazole:4-iodoimidazole was separated and its crystal structure was determined by X-ray diffraction techniques at 293 K/0.1 MPa. The structural analysis including the interplay between halogen-halogen interactions and NH···N hydrogen bonds was done including comparison with the known cocrystal.

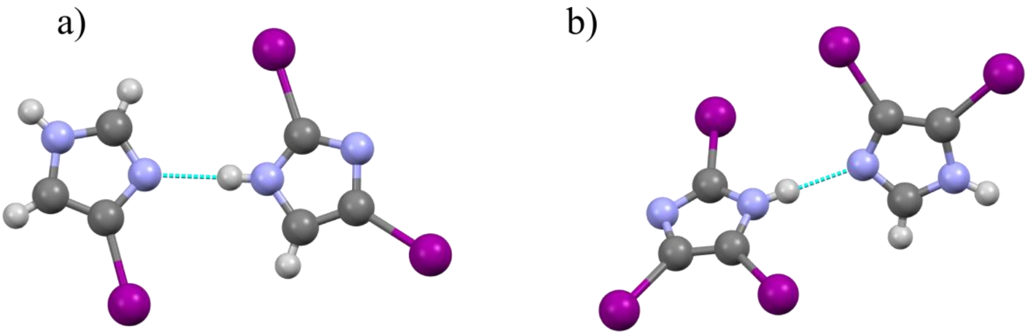


Figure 1: Crystal structures of iodinated imidazole cocrystals: a) 2,4-diiodoimidazole:4-iodoimidazole and b) 2,4,5-triiodoimidazole:4,5-diiodoimidazole.

Acknowledgements:
This study was supported by the Foundation for Polish Science, Team program 2009-4/6.

References
1. S. Childs, M.J. Zaworotko, Cryst. Growth Des., 9, 4529–4532, 2009
2. X. Ding, M. Tuikka and M. Haukka, Halogen bonding in crystal engineering, in: Recent advances in crystallography, Ed. Jason B. Benedict, InTech, 2012, pages: 153-154.

Structural diversities of charge transfer complexes

Michał A. Dobrowolski[1], *Kamila Pruszkowska*[1], *Patryk Rzepiński*[1], *Michał K. Cyrański*[1]

[1]*Faculty of Chemistry, Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland, miked@chem.uw.edu.pl*

Organic charge-transfer complexes show large variety of physical properties such as charge ordering, spin density waves (SDW) and superconductivity. Polycyclic aromatic hydrocarbons (PAHs) are typical examples of π-electron systems able to donate electron depending on their ionization potential *I*. 7,7,8,8-tetracyanoquinodimethane (TCNQ) is an example of an acceptor molecule which can be easily reduced to form the open shell electron radical $TCNQ^{\bullet -}$ when it is exposed to contact with electron donors. Benzenoid hydrocarbons containing in their crystal structures molecules of TCNQ exhibit semiconducting properties with a relatively small band gap and moderate charge-transfer between the counterions. Moreover, the electron transfer can be tuned by composition, stoichiometry, temperature or pressure. In this report we present synthesis and structural analyses of novel TCNQ complexes with two different benzenoid hydrocarbons (naphthalene and perylene or pyrene and perylene) in the crystal lattice. They both crystallize in triclinic P-1 space group and form face-to-face stacking between perylene and TCNQ molecules. Additionally we also present the structure of 1:1 TCNQ complexes with phenanthrene, pyrene or chrysene, which enabled us to estimate the degree of charge transfer in these kind of complexes.

D-Mannose structure at extreme conditions

Anna Jenczak[1], *Ewa Patyk*[1], *Andrzej Katrusiak*[1]

[1]*Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,*
Umultowska 89b, 61-614 Poznań, Poland, anna.jenczak@op.pl;

D-Mannose is monosaccharide of a great importance for proper functioning of a human organism and shows many useful properties, just to mention antiviral, antiparasitic, and antifungal activity. Similarly to other carbohydrates [1], significant number of OH groups makes it a good subject of study to analyze influence of extreme conditions on H-bond pattern.

Until now only crystal structure of α-D-mannopyranose [2] and unit-cell parameters for DL-mannose [3] were reported. In our study we have measured crystals and determined crystal structure of β-D-mannopyranose and studied its temperature and pressure behavior.

During first stage of our study single crystals of β-D-mannopyranose were measured in 150-295 K temperature range and then loaded to Merrill-Bassett Diamond-Anvil Cell (DAC) [4] and compressed up to 1.90 GPa. Pressure and temperature dependences of unit-cell parameters and volume were determined and changes in short-range interactions, OH···O hydrogen bonds and CH···O contacts, were investigated.

This study was supported by the TEAM grant No. 2009-4/6 from the Foundation for Polish Science.

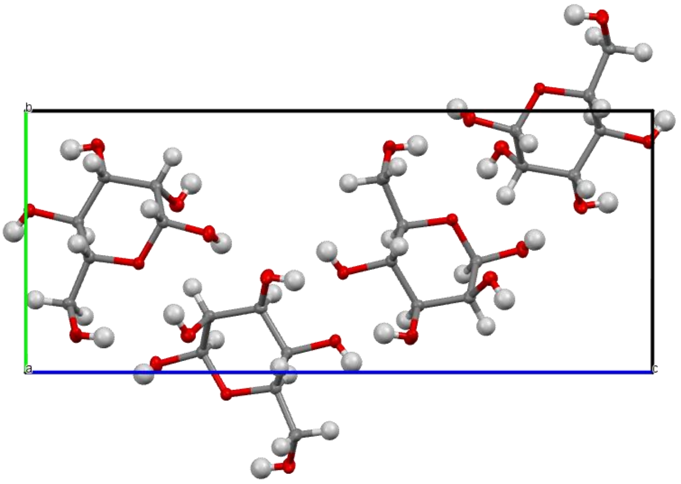


Fig. 1 Crystal structure of β-d-mannopyranose at 150 K shown along direction [100].

References

[1] Patyk, E.; Skumiel, J.; Podsiadlo, M.; Katrusiak, A. *Angew. Chem. Int. Ed.* **51** (2012) 2146-2150.

[2] Longchambon, F.; Avenel D.; Neuman A. *Acta Crystallogr. Sect. B-Struct. Sci.* **32** (1976) 1822-1826.

[3] Planinsek, F.; Rosenstein R.D. *ACS, Abstr.Papers (Summer)* (1967) 70.

[4] Merrill, L.; Bassett, W. A. *Rev. Sci. Instrum.* **45** (1974) 290-294.

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY

ADAM MICKIEWICZ UNIVERISTY POZNAŃ

FNP Foundation for Polish Science

EUROPEAN UNION

Why same of crystal structures are loose?

Michał Kaźmierczak[1], *Andrzej Katrusiak*[1]

[1] *Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, kax@amu.edu.pl*

Loose structures are crystal structures with all intermolecular contacts longer than the sum of van der Waals radii. These structures are relatively rare, survey of Cambridge Structural Database[1] revealed about 450 of such crystals[2].

These deposits can be classified and group by specific features. Almost all loose structures are molecular crystals, we can notice structures with low magnitudes of electrostatic potential on the molecular surface, indicative of a low contribution of electrostatic forces to the cohesion interactions. Molecules of crystalized substations are very often highly symmetric, bulky and substitute with large steric group (for example the most loose compound presently deposited in the CSD bis(trichlorosilyl)acetylene WILWUJ [3] shown in Fig. 1, the shortest of all contacts is by 0.256 Å longer than the sum of vdW radii).

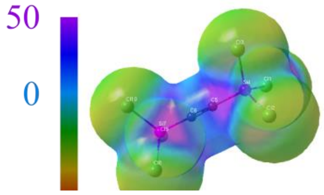


Fig. 1 Electrostatic potential distribution on the molecular isosurface (defined at 0.001) inbis(trichlorosilyl)acetylene (WILWUJ).

Loose crystals are relatively frequently higher-symmetric than all structures deposited in CSD (Fig. 2).

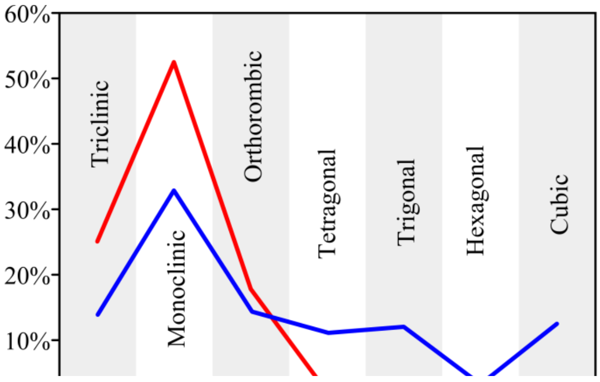


Fig.2 Percentage of all structures grouped according to crystallographic systems, for all structures in CSD (red line), and among the loosely packed crystals (blue line).

References

[1] Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* 2002, **58**, 380−388.
[2] Kaźmierczak, M.; Katrusiak, A. *J. Phys. Chem. C* 2013, **117**, 1441−1446.
[3] Rudinger, C.; Beruda, H.; Schmidbaur, H. *Z. Naturforsch., B:Chem.Sci.* 1994, **49**, 1348-1360

This study was supported by the Foundation for Polish Science, project TEAM

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY

ADAM MICKIEWICZ UNIVERSITY POZNAŃ

FNP
Foundation for Polish Science

EUROPEAN UNION

Inverse relationship of thermal expansion and compressibility rule in Ibuprofen

Magdalena Kropidłowska, Kinga Ostrowska, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Umultowska 89b, 61-614 Poznań, Poland, m.a.kropidlowska@gmail.com;

Ibuprofen [2(4-isobutylphenyl) propanoic acid, $C_{13}H_{18}O_2$] (Fig. 1) is a non-steroidal anti-inflammatory drug. It is currently available as a racemic mixture of S(+)-ibuprofen and R(-)-ibuprofen. The enantiomers (R and S) crystallizes in the monoclinic space group $P2_1$, (unit cell dimensions a=12.462 Å, b=8.035 Å, c=13.539 Å, β=112.89 °) [1]. The unit cell contains four ibuprofen molecules ($Z = 4$), with two molecules in the asymmetric unit ($Z' = 2$).
Racemic Ibuprofen has monoclinic symmetry with Z=4, space group $P2_1/c$ (unit cell a=14.667 Å, b=7.886 Å, c=10.730 Å and β=99.362°)[2].
(R,S)- Ibuprofen has been crystallized in a modified Merill-Bassett diamond anvil cell (DAC) [3] at pressure up to 1.28 GPa. We have also investigated the structure of the racemic compound at low temperature using X-ray single-crystal diffraction. Similarities and differences between the present and the literature data will be discussed.

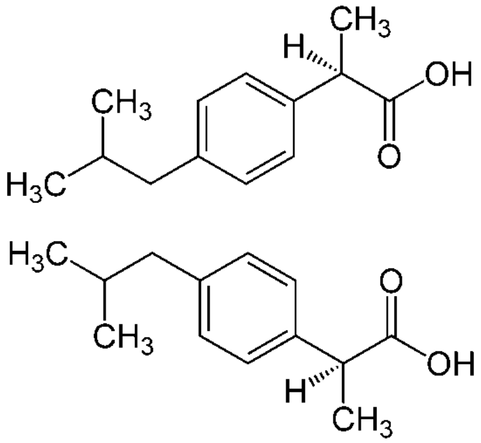


Fig 1. Enantiomers of Ibuprofen

References

[1] Freer, A. A., Bunyan, J. M., Shankland, N. & Sheen, D. B. *Acta Cryst. C* **49** (1993) 1378–1380.
[2] (a) McConnell, J. F. *Cryst. Struct. Commun*. **3** (1974) 73–75. (b) Shankland, N., Wilson, C. C., Florence, A. J. & Cox, P. J. *Acta Cryst. C* **53** (1997) 951–954.
[3] (a) Lawson, A. W.; Tang, T. Y. Rev. Sci. Instrum. **21** (1950) 815. (b) Jameson, J. C.; Lawson, A. W.; Nachtreib, N. H. Rev. Sci. Instrum. **30** (1959) 1016–1019. (c) Merrill, L.; Bassett, W. A. Rev. Sci. Instrum., **45** (1974) 290–294

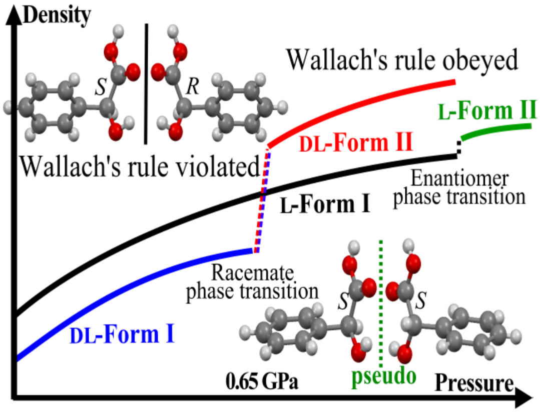
This study was supported by the Foundation for Polish Science, project TEAM

Mandelic acid vs the Wallach's rule

Jędrzej Marciniak, Michał Andrzejewski, Weizhao Cai, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Umultowska 89b, 61-614 Poznań, Poland, jedrzej.marciniak@amu.edu.pl;

At normal conditions, mandelic acid (MA) is an exempt from the Wallach's rule, as enantiomers L-MA and D-MA are denser than racemate DL-MA. However, the enantiomers are less compressible than the racemate, DL-MA, which additionally is anomalously compressed at the phase transition at 0.65 GPa and becomes more dense than the enantiomers. Our results exclude the possibility of resolving racemic DL-MA into enantiomers due to their higher density in a spontaneous crystallization induced by pressure up to 2.6 GPa at least. Also, the L-MA crystal undergoes an isostructural phase transition at 1.52 GPa, allowing a tighter packing of molecules mimicking a racemic arrangement. It is a general thermodynamic rule that pressure-induced phase transitions in racemates and enantiomers have the opposite effect for their densities relation and act toward or against the Wallach's rule, respectively.



References

[1] Brock, C.P.; Schweizer W.; Dunitz, J. D. On the validity of Wallach's rule: on the density and stability of racemic crystals compared with their chiral counterparts. *J. Am. Chem. Soc*. **1991**, 113 (26), 9811–9820.

[2] Jacques, J.; Collet, A.; Wilen, S. H.; Enantiomers, Racemates and Resolutions. Krieger Publishing Company: Malabar, FL. **1994**.

[3] Heo, J.; Mirkin, C. A. Pseudo-Allosteric Recognition of Mandelic Acid with an Enantioselective Coordination Complex. *Angew. Chem*. **2006**, 45 (6), 941-944.

[4] Rietveld, I. B.; Barrio, M.; Tamarit, J.-L.; Do, B.; Ceolin, R. Enantiomer Resolution by Pressure Increase: Inferences from Experimental and Topological Results for the Binary Enantiomer System (R)- and (S)-Mandelic Acid. *J. Phys. Chem. B* **2011**, 115, 14698−14703.

[5] Cai, W.; Marciniak, J.; Andrzejewski, M.; Katrusiak, A. Pressure Effect on d,l-Mandelic Acid Racemate Crystallization. *J. Phys. Chem. C* **2013**, 117, 7279-7285.

This study was supported by the Foundation for Polish Science, project TEAM

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY
ADAM MICKIEWICZ UNIVERSITY POZNAŃ
FNP Foundation for Polish Science
EUROPEAN UNION

High-pressure phases of urea

Kinga Ostrowska, *Andrzej Katrusiak*

Adam Mickiewicz University, Faculty of Chemistry,Umultiwska 89b, 61-614 Poznań, Poland ,

ostr@amu.edu.pl;

Single crystals of urea have been grown *in situ* at isothermal and isochoric conditions in a modified Merrill-Bassett diamond-anvil cell. [1] They were compressed to 3.10 GPa. Urea structure has been extensively studied by x-rays [2,3], neutrons [4], spectroscopy [3,5] and theory [6].

The transitions to the high-pressure phases take place at pressure near 0.5 GPa from phase I (tetragonal space group $P\bar{4}2_1m$) to phase III (orthorhombic space group $P2_12_12_1$). Above 2.80 GPa it's transforming to phase IV (orthorhombic space group $P2_12_12$).

The strong transformations of hydrogen bonds geometry and one two-center H_{anti}-bond breaking can be explained by molecular rearrangements induced by pressure. The onset of molecular rearrangements is induced by the collapse of the channel voids on the transformation to phase III, and then by the enforced close-packing alignment of the molecules on the transformation to phase IV. The molecular reorientations in urea phases I, III and IV and the changes of hydrogen-bonds dimensions, illustrate the importance of the angular dimensions and directionality of hydrogen bonds.

Physical origins of the spatial domains in phases III and IV are examined and discussed.

References

[1] (a) Lawson, A. W.; Tang, T. Y. *Rev. Sci. Instrum.* **1950,** *21*, 815. (b) Jameson, J. C.; Lawson, A. W.; Nachtreib, N. H. *Rev. Sci. Instrum.* **1959,** *30*, 1016–1019. (c) Merrill, L.; Bassett, W. A. *Rev. Sci. Instrum.*, **1974,** *45*, 290–294.

[2] Birkedal, M.; Madsen, D.; Mathiesen, R.; Knudsen, K.; Weber H-P.; Pattison, P.; Schwerzenbach, D. *Acta Crystallogr. Sect. A* **2004**, *60*, 371–381.

[3] Lamalas, F. J.; Dreger, Z. A.; Gupta, Y. M. *J. Phys. Chem. B* **2005**, *109*, 8206–8215.

[4] Guth, H.; Heger, G.; Klein, S.; Treutmann, W., Scheringer, C. *Z. Krystallogr.* **1980**, *153*, 237–254.

[5] Godfrey, P. D.; Brown, R. D.; Hunter, A. N. *J. Mol. Struct.* **1997,** *413-414*, 405–414.

[6] de Vries, R. Y.; de Veil, D.; Tsirelson V. *Acta Crystallogr. Sect. B.* **2000**, *56*, 118–123

This study was supported by the Foundation for Polish Science, project TEAM

INNOVATIVE ECONOMY NATIONAL COHESION STRATEGY

ADAM MICKIEWICZ UNIVERSITY POZNAŃ

FNP Foundation for Polish Science

EUROPEAN UNION

Short-range interactions of organic compounds at high pressure

<u>Ewa Patyk</u>[1], Andrzej Katrusiak[1]

[1]Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Umultowska 89b, 61-614 Poznań, Poland, ewapatyk@amu.edu.pl;

Some of the first high-pressure structures were determined for organic compounds.[1] Since then number of high-pressure crystallographic data raised significantly and is no longer limited to simple molecules but may be applied to complicated macromolecular systems. Pressure-induced changes of compressed crystals may lead to modification in hierarchy of short-range interactions and their thorough reorganization within the crystal structure.

Crystals of two simple organic compounds, sucrose [2] and pyridine N-oxide (PNO) [3], manifesting specific types of interactions, were studied at high pressure in order to investigate pressure-induced changes in short-range contacts. Two different approaches involving use of Merrill-Bassett Diamond-Anvil Cell (DAC) were applied to obtain crystals at high pressure. Ambient-pressure crystals of sucrose were isothermally compressed and isochoric high-pressure crystallization of liquid PNO residual was performed. Obtained crystals were measured with X-ray single crystal diffractometer.

Analysis of short-range interactions present in determined crystal structures of sucrose and PNO shown few interesting phenomena discussed in this presentation.

This study was supported by the TEAM grant No. 2009-4/6 from the Foundation for Polish Science.

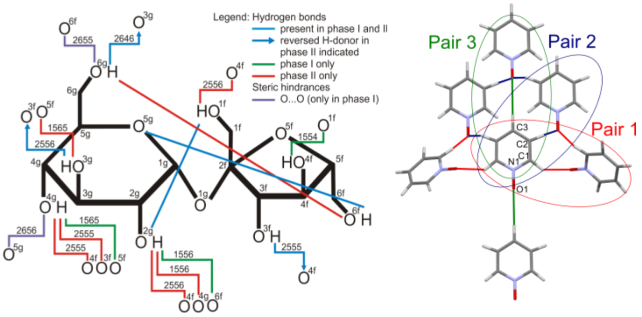


Fig. 1 Schemes of OH···O bonds pattern in sucrose (left) and CH···O contacts in PNO

References

[1] Piermarini, G.J.; Mighell, A.D., Weir, C.E., Block, S. *Science* **165 (**1969) 1250-1255.
[2] Patyk, E.; Skumiel, J.; Podsiadlo, M.; Katrusiak, A. *Angew. Chem. Int. Ed.* **51** (2012) 2146-2150.
[3] Patyk, E.; Marciniak, J.; Tomkowiak, H.; Katrusiak, A.; Merz, K. *Acta Crystallogr. Sect. B-Struct. Sci.- in admission*
[4] Merrill, L.; Bassett, W. A. *Rev. Sci. Instrum.* **45** (1974) 290-294.

High-pressure structural studies on 2,4,5-tribromo and 2,4,5-trichloroimidazole

Kacper Rajewski, Jędrzej Marciniak, Michał Andrzejewski, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,

Umultowska 89b, 61-649 Poznań, Poland, kacper.rajewski@gmail.com;

Structural stability of 2,4,5-tribromoimidazole (TBI) and 2,4,5-trichloroimidazole (TClI) was investigated with X-ray diffraction techniques in a modified Merril-Bassett high-pressure diamond-anvil cell (DAC) [1]. This is a useful instrument forphase-behavior studies in searching for new polymorphs and phase transitions. High-pressure investigations allowed determining compressibility of both substances. The comparative analysis of halogen-halogen interactions supporting hydrogen bonds was done for TBI and TClI in the function of pressure. Furthermore in situ crystallization of TBI above 0.5 GPa yields a double methylated imidazole bromide hydrate. Moreover subsequent recrystallization at 1.08 GPa led to dehydration and symmetry change. Pressure induced amine methylation was recently reported for dabco hydrobomine and hydroiodine salts [2]. Alkyl derivatives of imidazole are precursors for ionic liquid [3] what consider pressure techniques as their synthesis methods.

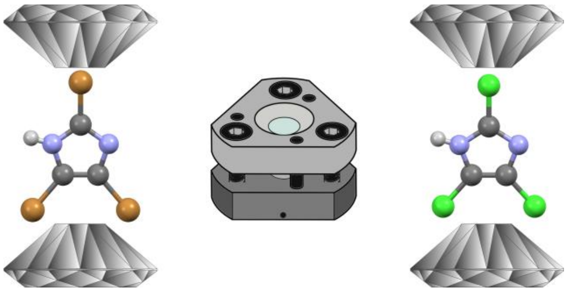


Figure 1: High-pressure investigations in a diamond-anvil cell.

Acknowledgements:

This work was supported by the Foundation for Polish Science, research project TEAM 2009-4/6.

References

[1]. L. Merrill, W. A. Bassett, Rev. Sci. Instrum., 1974, 45, 290–294.
[2]. M. Andrzejewski, A. Olejniczak, A. Katrusiak, CrystEngComm, 2012, 14, 6374-6376.
[3]. T. Welton, Chem. Rev., 1999, 99 (8), pp 2071–2084.

Pressure induced pinacolone crystallization - structural studies

Szymon Sobczak[1]*, Andrzej Katrusiak*[2]

[1]*Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland, szymonsobczak2@gmail.com;* [2]*Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland*

3,3-Dimethyl-2-butanone, commonly known as pinacolone, is formed through one of most basic rearrangements in organic chemistry. This pinacol rearrangement was first described in 1860 by Fittig and many examples of this reaction have been found since then [1]. The pinacol rearrangement takes place on heating the substrate in the presence of a strong acid, most often sulphuric acid. Recently, a non-catalytic high-pressure reaction of the pinacol rearrangement has been described. The reaction utilized supercritical water (scH2O) and was monitored by FTIR spectroscopy [2]. However, the pinacolone structure has not been determined yet. In situ high-pressure crystallizations were carried out in a diamond-anvil cell (DAC) [3,4]. Pinacolone at ambient conditions is liquid (mp. 283 K), however at 0.5 GPa plate-shaped single crystals are formed.

High-pressure X-ray diffraction studies on pinacolone revealed its molecular structure and intermolecular interactions.

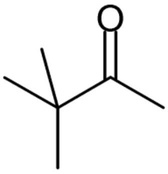


Fig. 1 Pinacolone (3,3-dimethyl-2-butanone).

References

[1] J. A. Berson, Angew. Chem. Int. Ed. 2002, 41, No. 24.

[2] Y. Ikushima, K. Hatakeda, O. Sato, T. Yokoyama, M. Arai, J. Am. Chem. Soc. 122 (2000) 1908.

[3] L. Merrill, W. A. Bassett, Rev. Sci. Instrum. 45 (1974) 290.

[4] A. Katrusiak, *Acta Cryst.*. **A64** (2008) 135.

This study was supported by the Foundation for Polish Science, project TEAM

Pyridine N-oxide at high-pressure

Hanna Tomkowiak, Ewa Patyk, Jędrzej Marciniak, Andrzej Katrusiak

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Umultowska 89b, 61-614 Poznań, Poland, hannat@amu.edu.pl

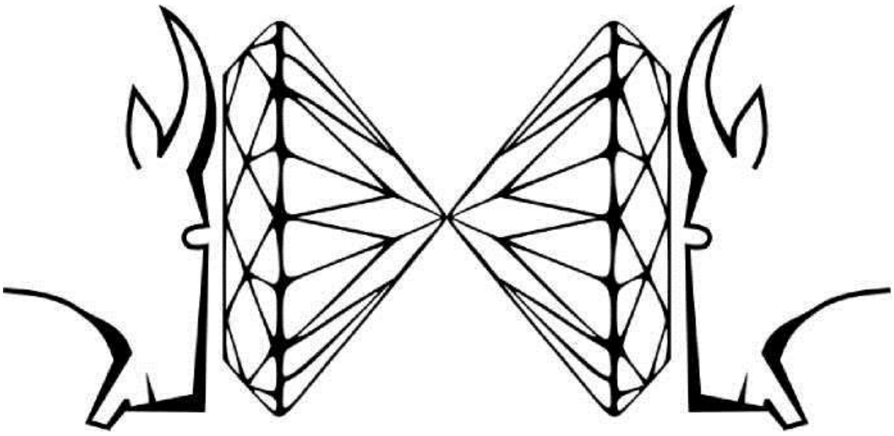
Pyridine N-oxide (PNO), C_5H_5NO, is crystalline at ambient conditions and melts at 341 K [1]. PNO crystals are highly hygroscopic and dissolve when exposed to air atmosphere, but they can be easily crystallized in the neat form of the aqueous solution at high-pressure.

Single crystals of PNO have been *in situ* grown in a Merrill-Bassett diamond-anvil cell (DAC) [2] and their structures were determined by X-ray diffraction. High-pressure crystallizations of PNO at isochoric conditions lead to the same crystal phase as the one at ambient conditions. Systematic extinctions clearly indicate~~s~~ the tetragonal system. High-pressure crystals have symmetry of space group $P4_12_12$ ($a = b = 5.6634(8)$ Å, $c = 13.6450(27)$ Å, $V = 437.65(12)$ Å^3). PNO crystal structure is stabilized by C-H···O contacts. The crystal compression and thermal expansion as well as three shortest H···O distances comply with the inverse-relationship rule of pressure and temperature changes.

This study was supported by the TEAM grant No. 2009-4/6 from the Foundation for Polish Science.

References

[1] Klyuchnikov, O. R., Saifullin, I. Sh., Nikishev, Yu. Yu. (1994). *Chemistry of Heterocyclic Compounds*, **30**, 564–566.
[2] Merrill, L. & Bassett, W. A. (1974). *Rev. Sci. Instrum*., **45**, 290–294.



Laboratory work

High-pressure laboratories

Anna Olejniczak, Marcin Podsiadło

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland, aniao@amu.edu.pl, marcinp@amu.edu.pl

High-pressure technique is a convenient tool for crystallization and it is becoming more popular. First devices used for high-pressure experiments were big and the access to the studied substance was limited.[1] The next step was applying diamonds for generating high pressure.[2, 3] A breakthrough was inventing miniature diamond anvil cell in 1974 [4] and applying a ruby fluorescence method for pressure calibration.[5] Since then the diamond anvil cell (DAC) has become a convenient device for high-pressure experiments. It is a small, relatively cheap and save apparatus, suitable for diffraction structural studies, spectroscopy and many other types of physical measurements. Application of DAC enables people to learn and to understand the behavior of different substances in extreme conditions and the nature of intermolecular interactions. It also used for synthesizing new materials, polymorphs and solvates, that are difficult to obtain at normal conditions. Very often high-pressure experiments are more convenient than the low-temperature measurements and give the opportunity to choose the crystallization method (isothermal, isochoric).[6]

High-pressure laboratories involve practical exercises with the diamond-anvil cell (DAC), its assembling and loading with samples, centering the DAC on a CCD diffractometer, diffraction data collection and processing. Isothermal and isochoric crystallizations will be applied for growing single crystals of new phases of substances brought in by participants. The laboratories will include theoretical and practical parts for both beginner and expert high-pressure crystallographers. The aim of this workshop is to encourage the participants to start high-pressure experiments in their laboratories.

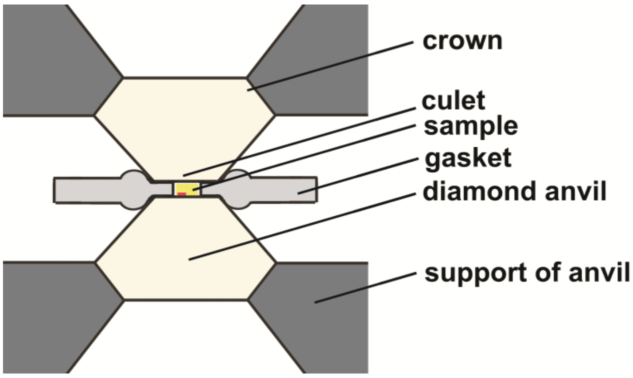


Fig. 1 Schematic cross-section of the diamond-anvil cell: the diamond anvils, mounted on the steel supporting plates, plastically deforming the metal gasket, and compressing the hydrostatic fluid filling inside the centrally located chamber (a hole in the gasket). The fluid transmits pressure to the sample and to a piece of ruby for spectroscopic pressure calibration.

References

[1] Bridgman, P.W. *Review of Modern Physics* **18** (1946) 1-95.
[2] Lawson, A.W.; Tang, T.Y. *Rev. Sci. Instrum.* **21** (1950) 815-815.
[3] Jamieson, J.C.; Lawson, A.W.; Nachtrieb, N.D. *Rev. Sci. Instrum.* **30** (1957) 1016-1019.
[4] Forman, R.A.; Piermarini, G.J.; Barnett, J.D.; Block, S. *Science* **176** (1972) 284-285.
[5] Merrill, L.; Bassett, W.A. *Rev. Sci. Instrum.* **45** (1974) 290-294.
[6] Katrusiak, A. *Acta Cryst.* **A64** (2008) 135-148.