

MS24-04 High Pressure / Low Temperature Polymorphism in Simple Aromatic Systems. Joe Ridout, Michael R. Probert, University of Durham, United Kingdom.
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It is well known that application of pressure to a material can have a very different effect to reducing its temperature. This phenomenon is far from being well understood. For cubic systems isothermic and isobaric compression are directly related. However, in systems of lower symmetry the anisotropy of structural strain on cooling may be similar or very different, possibly leading to high pressure / low temperature polymorphism.[1]

The lack of previously reliable and accurate method of phase prediction tools has been described as “a continuing scandal” by John Maddox.[2] Significant progress has taken place in the two decades since this oft-quoted phrase was penned, and it is now possible for crystal prediction tools to calculate the crystal energy landscape for materials and find and even predict polymorphic tendencies.[3]

We believe that our studies investigating non ambient crystallisation induced polymorphism may provide insights into why materials behave very differently under low temperature and high pressure conditions. Furthermore, such studies have the potential to produce useful data points for phase prediction tools and it remains interesting to see whether the observed polymorphism can be predicted using such methods.

2-, 3-, and 4- regioisomers of fluorotoluene, liquids at ambient conditions, have been crystallised using the minimum possible application of two distinct in-situ methods: Cryo-crystallisation (LT) and through the application of high-pressure (HP). We observe that in two of the three fluorotoluenes the HP and LT crystalline forms are entirely distinct. The packing efficiencies of the HP phases were found to be considerably greater than that of the LT phases.

In addition, we will present the unique single-crystal facilities available at Durham; the XIPHOS diffraction facility, which has been designed to bridge the gap between home laboratory and central facilities equipment. XIPHOS has been developed for measurements in the ultra low temperature range (1.9K) [4], while XIPHOS II has been developed specifically for use in high-pressure experiments. The short wavelength Ag X-radiation employed on XIPHOS II has lower absorption and allows for greater data collection at high-resolution within the geometrical confines created by the DAC. Multilayer focusing optics have achieved high flux densities at very low powers (30 W) and the microfocus beam reduces unwanted diffraction from both the body of the DAC and the metal gasket. [5]

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MS24-05 An entire class of compounds forming polar crystals and showing single-crystal-to-single-crystal transitions between polar phases. Roberto Centore,^a Mojca Jazbinsek,^b Angela Tuzi,^a Andrea Peluso,^c Amedeo Capobianco,^c ^a Department of Chemical Sciences, University of Naples “Federico II”, Italy, ^b Nonlinear Optics Laboratory, ETH Zürich, Switzerland, ^c Dipartimento di Chimica e Biologia, Università di Salerno, Italy.
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In a polar crystal there is a direction that is not transformed in the opposite direction by any symmetry operation of the crystal class. That direction is called the polar axis of the crystal [1]. Polar crystal structures are in general rare. As a matter of fact, all centrosymmetric crystals are non-polar but only 10, out of the 21 crystal classes lacking the center of symmetry, are polar. Among achiral organic compounds only 10-15 % crystallize in non-centrosymmetric space groups. This finding is consistent with the classic analysis of Kitaigorodsky, who showed that many space groups allowing the close packing of molecules are centrosymmetric [2]. Polar crystals are of great interest and abiding wanted because some physical properties represented by odd-rank tensors and highly requested in materials for advanced applications, such as pyroelectricity, ferroelectricity, piezoelectricity, second harmonic generation, electrooptical response, are only allowed or they are enhanced in polar crystal structures [1].

In this communication we show that condensation of 4-hydroxybenzohydrazide with a variety of non-chiral aliphatic ketones such as methylethylketone, acetone, cyclohexanone and cyclobutanone, affords imine compounds crystallizing in polar space groups (*Pna2₁* or *Cc*) [3]. For all the compounds synthesized, the crystal structure was determined by single crystal X-ray analysis and second harmonic generation experiments were performed on powder samples. The imine obtained using acetone shows solid state polymorphism with unusual behaviour; three different crystal phases have been identified (phases I, II and III), all having the same polar space group *Pna2₁*, and the transitions from I to II and from III to II, are topotactic, *i.e.* single-crystal-to-single-crystal. During the irreversible transition from phase I to II, the polar axis undergoes a strong compression (about 15 %) and single crystals of the parent phase are violently shattered in single crystal fragments of the new phase, while in the reversible transition from phase III to II, the polar axis expands (about 14 %) and the integrity of single crystals is preserved. Our results provide a new and striking example of the fascinating and still poorly understood thermosalient effect [4].

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